

THE CALCULATION OF LIMITS OF  
DETECTABILITY AND OPTIMUM CONDITIONS  
FOR ATOMIC EMISSION AND ABSORPTION  
FLAME SPECTROMETRY

By  
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# KEY TO SYMBOLS

|                   |                                                           |
|-------------------|-----------------------------------------------------------|
| A                 | effective aperture of the monochromator, cm. <sup>2</sup> |
| a                 | damping constant, no units                                |
| A <sup>0</sup>    | absorbance, no units                                      |
| A <sub>T</sub>    | total absorption of spectral line, no units               |
| A <sub>t</sub>    | transition probability, sec. <sup>-1</sup>                |
| A <sub>α</sub>    | 1 - I/I <sup>0</sup> , no units                           |
| A <sub>ν</sub>    | atomic absorptivity at frequency ν, no units              |
| B                 | factor characteristic of photodetector surface, no units  |
| B <sub>e</sub>    | rotational constant of molecule cm. <sup>-1</sup>         |
| B(T)              | partition function, no units                              |
| C                 | concentration, moles/liter                                |
| c                 | speed of light, 3 x 10 <sup>10</sup> cm./sec.             |
| C <sub>i</sub>    | constant defined in text                                  |
| D                 | angular dispersion, radians/mm                            |
| D <sub>NaCl</sub> | dissociation energy of NaCl, electron volts               |
| e                 | base of natural logarithms, no units                      |
| E <sub>i</sub>    | energy of state i, electron-volts                         |
| e <sub>c</sub>    | electronic charge, 1.59 x 10 <sup>-19</sup> coulombs      |
| e <sub>f</sub>    | expansion factor, no units                                |
| F                 | focal length of collimator, cm.                           |
| Δf                | frequency response band width, sec. <sup>-1</sup>         |
| G                 | gain per stage of photomultiplier, no units               |

|                         |                                                                                                                       |
|-------------------------|-----------------------------------------------------------------------------------------------------------------------|
| $g_1$                   | statistical weight of state 1, no units                                                                               |
| $g_0^1$                 | statistical weight of ground state of ion, no units                                                                   |
| $g_0^*$                 | statistical weight of ground state of molecule, no units                                                              |
| $H$                     | slit height, cm.                                                                                                      |
| $h$                     | Planck's constant, $6.62 \times 10^{-27}$ erg-sec./atom                                                               |
| $I$                     | integrated intensity, watts/cm. <sup>2</sup> ster.                                                                    |
| $i$                     | output signal, amperes                                                                                                |
| $I^0$                   | transmitted intensity with no sample in flame, watts/cm. <sup>2</sup> ster.                                           |
| $i^0$                   | signal due to $I^0$ , amperes                                                                                         |
| $\overline{\Delta I^0}$ | r.m.s. fluctuation in $I^0$ , watts/cm. <sup>2</sup> ster. sec. <sup>-1/2</sup>                                       |
| $\overline{\Delta i^0}$ | noise signal due to fluctuations in $I^0$ , amperes                                                                   |
| $I_c$                   | intensity of the flame continuum, watts/cm. <sup>2</sup> ster. mp                                                     |
| $i_c$                   | signal due to $I_c$ , amperes                                                                                         |
| $\overline{\Delta I_c}$ | root-mean-square fluctuation of intensity of flame continuum,<br>watts/cm. <sup>2</sup> ster. mp sec. <sup>-1/2</sup> |
| $\overline{\Delta i_c}$ | noise signal due to fluctuation of flame continuum, amps.                                                             |
| $i_d$                   | dark current, amps.                                                                                                   |
| $I_e$                   | intensity of thermal emission of the line of interest,<br>watts/cm. <sup>2</sup> ster.                                |
| $i_e$                   | signal due to $I_e$ , amperes                                                                                         |
| $\overline{\Delta I_e}$ | r.m.s. fluctuation in $I_e$ , watts/cm. <sup>2</sup> ster. sec. <sup>-1/2</sup>                                       |
| $\overline{\Delta i_e}$ | noise signal due to fluctuation in $I_e$ , amperes                                                                    |
| $I_f$                   | intensity of fluorescent emission of the lines of interest,<br>watts/cm. <sup>2</sup> ster.                           |
| $i_f$                   | signal due to $I_f$ , amperes                                                                                         |
| $i_i$                   | chemical constant of species i, no units                                                                              |
| $I_m$                   | intensity due to $N_m$ , watts/cm. <sup>2</sup> ster.                                                                 |
| $i_m$                   | output signal due to $N_m$ , amps.                                                                                    |
| $\overline{\Delta i_p}$ | phototube noise signal, amps.                                                                                         |



|                         |                                                                                                                |
|-------------------------|----------------------------------------------------------------------------------------------------------------|
| $i_s$                   | signal due to scattered incident radiation, amperes                                                            |
| $\overline{\Delta I_s}$ | r.m.s. fluctuation in intensity of scattered radiation,<br>watts/cm. <sup>2</sup> ster. sec. <sup>-1/2</sup>   |
| $\overline{\Delta i_s}$ | noise signal due to fluctuation in scattered incident<br>radiation, amperes                                    |
| $I_t$                   | transmitted intensity with sample in flame, watts/cm. <sup>2</sup> ster.                                       |
| $i_t$                   | signal due to $I_t$ , amps.                                                                                    |
| $\overline{\Delta i_T}$ | total noise signal, amps.                                                                                      |
| $I_\nu^B$               | intensity of a black body radiator at frequency $\nu$ , watts/cm. <sup>2</sup><br>ster.                        |
| $I_{\nu_0}^B$           | intensity of a black body radiator at frequency $\nu_0$ ,<br>watts/cm. <sup>2</sup> ster.                      |
| $k$                     | Boltzmann constant, see units in text                                                                          |
| $k^0$                   | atomic absorption coefficient at the line center, cm. <sup>-1</sup>                                            |
| $k_m^0$                 | atomic absorption coefficient at the line center at the<br>minimum detectable concentration, cm. <sup>-1</sup> |
| $k_0^*$                 | atomic absorption coefficient at the line center for a pure<br>Doppler broadened line, cm. <sup>-1</sup>       |
| $K_c$                   | constant defined in text                                                                                       |
| $K_H$                   | dissociation constant for HCl, atm.                                                                            |
| $K_s$                   | constant defined in text                                                                                       |
| $k_c$                   | $k_8 k_9 / \overline{\Delta i_T}$                                                                              |
| $k_d$                   | $k_8 k_{11} / \overline{\Delta i_T}$                                                                           |
| $K_1$                   | dissociation constant for NaCl, atm.                                                                           |
| $K_2$                   | ionization constant for Na, atm.                                                                               |
| $K_3$                   | dissociation constant for NaOH, atm.                                                                           |
| $k_1$                   | $\chi T_f H(A/F^2) nI$                                                                                         |
| $k_2$                   | $2BMe_c \Delta f$                                                                                              |
| $k_3$                   | $\chi T_f H(A/F^2) I_c$                                                                                        |
| $k_4$                   | $\chi T_f H(A/F^2) \overline{\Delta I_c}$                                                                      |
| $k_5$                   | $\chi T_f H(A/F^2) I^0 (1 - e^{-\rho k^0 L})$                                                                  |

$$k_6 \quad \gamma T_f H(A/F^2)$$

$$k_7 \quad (2BMe_c I^0) / (\gamma T_f HA/F^2)$$

$$k_8 \quad \gamma T_f H(A/F^2) \quad n \quad \left[ \frac{2BMe_c i_d}{(\gamma T_f H(A/F^2) (\Delta f)^{1/2} R_d)^2} \right]$$

$$k_9 \quad \frac{h \nu_o g_u}{4\pi \times 10^7 B(T)} A_t$$

$$k_{10} \quad \frac{h \nu_o^2}{10^7 c} \left( \frac{\Delta \nu_D g_u}{\pi \sqrt{\ln 2} B(T)} A_t a \right)^{1/2}$$

$$k_{11} \quad \frac{h \nu_o A_t}{10^7 4\pi B(T)} (K_1 g_1 + K_2 g_2)$$

$$k_{12} \quad \frac{h \nu_o^2}{10^7 c} \frac{\Delta \nu_D a A_t}{\pi \sqrt{\ln 2} B(T)} \left[ K_1 (g_1)^{1/2} + K_2 (g_2)^{1/2} \right]$$

$$k_{13} \quad \left[ (\overline{I^0}/I^0) (\Delta f)^{1/2} \right]^{-1}$$

$$k_{14} \quad \frac{\rho 2 \sqrt{\ln 2} \lambda_o^2 g_u A_t \delta c M_a^{1/2}}{\sqrt{\pi} 8\pi B(T) 2 \sqrt{2} R \ln 2 \nu_o}$$

$$k_{15} \quad \frac{\Theta 2 \sqrt{\ln 2} \lambda_o^2 (g_1 + g_2) c M_a^{1/2} A_t \delta}{\sqrt{\pi} 8\pi B(T) 2 \sqrt{2} R \ln 2 \nu_o}$$

k atomic absorption coefficient at  $\nu$  other than  $\nu_o$ , cm.<sup>-1</sup>

L flame diameter, cm.

M amplification factor of photodetector, no units

M<sub>a</sub> atomic weight, atomic mass units

M<sub>f</sub> effective molecular weight of foreign species, atomic mass units

M<sub>NaCl</sub> molecular weight of NaCl, atomic mass units

N total atomic concentration of species of interest, atom/cm.<sup>3</sup>

n entrance optics factor, no units

N<sup>0</sup> ground state concentration of species of interest, atoms/cm.<sup>3</sup>

N<sub>f</sub> concentration of foreign species, particles/cm.<sup>3</sup>

N<sub>i</sub> atomic concentration at intersection (self-absorption) point, atoms/cm.<sup>3</sup>

N<sub>m</sub> minimum detectable number of atoms/cm.<sup>3</sup> of flame gases

|                       |                                                                         |
|-----------------------|-------------------------------------------------------------------------|
| $N_m^0$               | ground state minimum detectable concentration, atoms/cm. <sup>3</sup>   |
| $n_T$ ,<br>$n_{298}$  | moles present at temperature T and temperature 298°K.,<br>respectively  |
| P                     | power, watts                                                            |
| $P_a$                 | pressure of species of interest, mm.                                    |
| $P_{Cl}$              | partial pressure of Cl in all forms, atm.                               |
| $P_e$                 | partial pressure of electrons in the flame, atm.                        |
| $P_e$                 | partial pressure of electrons due to ionization of flame gases,<br>atm. |
| $P_f$                 | pressure of foreign species, mm.                                        |
| $p_i$                 | partial pressure of species i, atm.                                     |
| $P_T$                 | total pressure of species of interest in all forms, atm.                |
| Q                     | flow rate of unburned gases, cm. <sup>3</sup> /sec.                     |
| R                     | gas constant, $8.3 \times 10^7$ ergs/mole°K.                            |
| $R_d$                 | reciprocal linear dispersion, mμ/cm.                                    |
| $R_f$                 | reflectance of optics, no units                                         |
| $R_O$                 | resistance of load resistor, ohms                                       |
| s                     | spectral slit width, mμ                                                 |
| $s_a$                 | spectral slit width due to aberrations, coma, etc., mμ                  |
| $s_c$                 | $s_d + s_a$ , mμ                                                        |
| $s_d$                 | diffraction limited spectral slit width, mμ                             |
| $s_m$                 | spectral slit width as determined by mechanical slit width, mμ          |
| T                     | flame temperature, °K.                                                  |
| $\overline{\Delta T}$ | root-mean-square temperature fluctuation, °K.                           |
| $T_f$                 | transmission factor of optics, no units                                 |
| $T_m$                 | transmittance of flame, no units                                        |
| $T_O$                 | temperature of load resistor                                            |
| V                     | ionization energy of atom, electron volts                               |

|              |                                                                                                                                           |
|--------------|-------------------------------------------------------------------------------------------------------------------------------------------|
| $v$          | $\frac{2(\nu - \nu_0)}{\Delta \nu_D} \sqrt{\ln 2}$ , no units                                                                             |
| $W$          | slit width, cm.                                                                                                                           |
| $W_0$        | optimum slit width, cm.                                                                                                                   |
| $y$          | $\frac{2\Delta}{\Delta \nu_D} \sqrt{\ln 2}$ , no units                                                                                    |
| $Z_H$        | number of Holtsmark broadening collisions/sec. atom                                                                                       |
| $Z_L$        | number of Lorentz broadening collisions/sec. atom                                                                                         |
| $\alpha$     | ratio of emission line width to absorption line width, no units                                                                           |
| $\alpha_0$   | width of beam of radiation at dispersing element, cm.                                                                                     |
| $\beta$      | fraction to account for incomplete compound formation and atomic losses due to ionization, no units                                       |
| $T_i$        | abundance of isotope i, no units                                                                                                          |
| $\gamma$     | photosensitivity factor, amps./watt                                                                                                       |
| $\Delta$     | a variable distance from the point $\nu - \nu_0$ , sec. <sup>-1</sup>                                                                     |
| $\delta$     | factor to account for line broadening other than Doppler broadening at $\nu = \nu_0$ , no units                                           |
| $\delta_\nu$ | factor to account for line broadening other than Doppler broadening at $\nu$ other than $\nu_0$ , no units                                |
| $\epsilon$   | atomization efficiency, no units                                                                                                          |
| $\xi$        | statistical weight fraction, no units                                                                                                     |
| $\eta_i$     | ratio of intensity of hyperfine component i to the sum of the intensities of all other hyperfine components due to nuclear spin, no units |
| $\Theta$     | correction factor to account for multiplicity of spectral line, no units                                                                  |
| $\kappa$     | slit function parameter, no units                                                                                                         |
| $\lambda$    | wavelength setting of monochromator, cm.                                                                                                  |
| $\lambda_0$  | wavelength at line center, cm.                                                                                                            |
| $\nu$        | frequency, sec. <sup>-1</sup>                                                                                                             |
| $\nu_0$      | frequency at line center, sec. <sup>-1</sup>                                                                                              |

|            |                                                                                                                |
|------------|----------------------------------------------------------------------------------------------------------------|
| $\xi$      | ratio of root-mean-square fluctuation in the background intensity to background intensity, sec. <sup>1/2</sup> |
| $\pi$      | 3.14, no units                                                                                                 |
| $\rho$     | correction factor to account for hyperfine structure of source and absorption line, no units                   |
| $\sigma_H$ | cross section for Holtsmark broadening, cm. <sup>2</sup>                                                       |
| $\sigma_L$ | cross section for Lorentz broadening, cm. <sup>2</sup>                                                         |
| $\tau$     | lifetime of an excited state, seconds                                                                          |
| $\phi$     | flow rate of solution, cm. <sup>3</sup> /min.                                                                  |
| $\chi$     | $\overline{\Delta I^0}/I^0$ , sec. <sup>1/2</sup>                                                              |
| $\psi$     | $\overline{\Delta I_e}/I_e$ , sec. <sup>1/2</sup>                                                              |
| $\omega_e$ | vibrational constant of molecule, cm. <sup>-1</sup>                                                            |
| $\omega_i$ | $T_i h_i$ , no units                                                                                           |

## I. INTRODUCTION

The selection of optimum conditions is a problem which confronts every analyst. To the analyst using atomic emission and atomic absorption flame spectrometry this problem is particularly vexing. Trial-and-error methods of choosing optimum conditions are tedious and often misleading because of the large number of variables and their interdependence, and, until the present time, no adequate treatment has been given describing the quantitative relationship of experimental factors to the sensitivity of analysis. The work reported here was begun as an attempt to take a more systematic and quantitative approach to the question of optimum conditions for flame spectrometric analysis. However, the theoretical principles and expressions developed in this paper have wider applicability than the prediction of optimum conditions and, in fact, should provide the means for a quantitative discussion of many of the phenomena and interferences so frequently encountered in flame spectrometry.

It is hoped that two major purposes will be served by this study: first, to demonstrate that the influence of experimental variables on the measured signal in atomic emission and atomic absorption flame spectrometry can be treated quantitatively in a relatively simple manner, and, second, that from this treatment optimum conditions of analysis can be selected. It should be clear that if these purposes are achieved this study will provide information of aid in routine analysis as well as in theoretical considerations.



The approach taken in this study is to write expressions for the signal and the noise as functions of the experimental parameters for atomic emission and atomic absorption flame spectroscopy. The limit of detectability is then defined as the atomic concentration of the species of interest which gives a signal-to-noise ratio equal to two. The resulting expression for the limit of detectability makes possible the estimation of the effect of various experimental parameters on the sensitivity of analysis and also allows a direct calculation of the limit of detectability which may be expected. The selection of optimum conditions for any concentration range of the species of interest is discussed on the basis of a maximum signal-to-noise ratio. The effects of compound formation and ionization of the species of interest and self-absorption of radiation are considered. Using the derived expressions the calculation of optimum conditions is carried out for the atomic emission flame spectrometric analysis of sodium, and the results of the theory are compared with experimental measurements.

## II. CALCULATION OF THE LIMIT OF DETECTABILITY FOR ATOMIC EMISSION FLAME SPECTROMETRY

### Introduction

The system under consideration in the development of this theory consists of a flame source, a lens or mirror for focusing the emitted radiation on the monochromator entrance slit, a monochromator with accompanying optics and slits, a photodetector, amplifier, and readout (recorder, meter, etc.). For the purposes of the theory, it is assumed that the source is aligned for maximum intensity and that the slit is fully and uniformly illuminated. The following discussion will apply to either flames produced using total consumption or chamber type atomizer-burners. However, when using atomizer-burners, flames are far from homogeneous, and so it will be assumed that the brightest part of the outer cone of the flame is always selected for viewing. For purposes of simplicity the dimensions of the entrance and exit slits are assumed to be the same, although, where the two slits are separately adjustable, a small gain in sensitivity may result by having the exit slit slightly larger than the entrance slit. The width and height of the slits are, respectively,  $W$  and  $H$ . The effective aperture of the monochromator is  $A$ , cm.<sup>2</sup>, and the focal length of the collimator lens or mirror is  $F$ , cm. The term  $T_f$  is the transmission factor of the spectrometric system (includes entrance optics as well as monochromator optics) as determined by absorption and reflection losses at all optical surfaces.



The spectral slit width of the monochromator is denoted  $s$  and is given (6,8,29) approximately by

$$s = s_m + s_d + s_a = s_m + s_c, \quad [1]$$

where  $s_m$  is the spectral slit width of the monochromator when using wide slits,  $s_d$  is the diffraction limited spectral slit width of the monochromator assuming focusing aberrations are negligible,  $s_a$  is the spectral slit width of the monochromator due to coma, aberrations, imperfect optics, mismatch of slit curvature, etc., which results in a circle of confusion of constant size at the exit slit, and  $s_c = s_d + s_a$ . In this paper the spectral slit width will always have units of  $m\mu$ . The terms  $s_m$  in  $m\mu$  is given (8,29) by

$$s_m = (1/DF)W = R_d W, \quad [2]$$

where  $D$  is the angular dispersion of the monochromator in radians per  $m\mu$ , and  $R_d$  is the reciprocal linear dispersion of the monochromator in  $m\mu$  per cm. (i.e., A. per mm.). The term  $s_d$ , in  $m\mu$ , is given (8,29) by

$$s_d = (1/D)\lambda/\alpha_0 = FR_d\lambda/\alpha_0, \quad [3]$$

where  $\lambda$  is the wavelength setting of the monochromator in cm., and  $\alpha_0$  is the width of the beam of radiation in cm. at the dispersing element. The term  $s_a$ , in  $m\mu$  units, is a constant characteristic of the monochromator.

Equation [1] is not strictly correct because the above effects are not strictly additive (6). However, equation [1] will give the correct value of the spectral slit width when any one of the terms predominates. If the above effects are of the same magnitude and are

independent, then the spectral slit width,  $s$ , will be given more accurately by Pythagorean addition, i.e.,  $s^2 = s_m^2 + s_c^2$ . In this section the additive relationship for  $s$ , given in equation [1], will be used.

In addition to the above requirements concerning the entrance optics and the monochromator, the following requirements will be made for the system under consideration. It will be assumed that the detector intercepts all the radiation passing through the exit slit and that the amplifier-readout system is well regulated so that the limiting noise is a result of detector and flame noise. The above assumptions and requirements regarding the instrumental system to be used are generally valid for any good commercial flame spectrometer; and, therefore, the following discussion should be directly applicable to many experimental systems.

#### Derivation of Equations

The minimum detectable concentration,  $N_m$ , will be defined as that concentration which produces an average output current (anodic current of phototube)  $i_m$ , in amperes, such that

$$i_m = 2 \overline{\Delta i_T} , \quad [4]$$

where  $\overline{\Delta i_T}$  is the root-mean-square fluctuation in the background anodic current of the phototube. The value of  $i_m$  is given (20) by

$$i_m = K \gamma T_f I_m W H (A/F^2) n , \quad [5]$$

where  $\gamma$  is the photosensitivity factor, i.e., the current in amperes produced at the anode of the detector for each watt of radiant power incident upon the photocathode, and  $I_m$  is the total intensity (integrated

intensity) of the spectral line (in watts/cm.<sup>2</sup> ster.) produced by the minimum detectable concentration. (More correctly,  $I_m$  should be called the steradiancy (32) of the spectral line, but the more general term "intensity" is used throughout with the units carefully specified.)

The term  $A/F^2$  is the number of steradians viewed by the spectrometric system as long as the effective aperture is filled with radiation. This is true whether the source is viewed directly or a lens or mirror is used to focus a selected portion of the flame on the slit. The parameter  $n$  is the number of solid angles of value  $A/F^2$  which are gathered into a single solid angle by means of a suitable arrangement of entrance optics. As has been pointed out by Gilbert (17), it is possible by the use of a suitable system of mirrors to increase the intensity incident upon the spectrometric system. Thus, if a mirror is suitable placed so as to focus an additional image of the source on the slit, then the total incident intensity is increased by  $n = 1 + R_f T_m$  where  $R_f$  is the reflectance of the mirror and  $T_m$  is the transmittance of the flame for the particular spectral line in concern. Using the spectrometric system which is described at the beginning of this section, a single viewing ( $n = 1$ ) of the flame is assumed. Once a theory is worked out for a single viewing of the flame source, it is easy to evaluate  $n$  for any number of viewings by proper consideration of the geometry of the entrance optics. Gilbert (17) has considered several possible optical arrangements for increasing the light gathering power.

The parameter  $K$  accounts for the position of the spectral line with respect to the slit function distribution curve. For equal entrance and exit slits, the distribution curve is triangular, and the slit function parameter is given (8) by

$$\kappa = 1 - \frac{|\lambda - \lambda_0|}{s}, \quad [6]$$

where  $\lambda$  is the wavelength setting of the monochromator, and  $\lambda_0$  is the wavelength of the line center. For monochromator wavelengths greater than  $\lambda_0 + s$  and less than  $\lambda_0 - s$ ,  $\kappa$  is zero. If the monochromator has sufficient resolution to isolate a single, sharp spectral line, then the value of  $\kappa$  can be made equal to unity by adjusting the monochromator wavelength,  $\lambda$ , to the peak wavelength of the spectral line,  $\lambda_0$ .

The integrated intensity  $I_m$  in units of watts/cm.<sup>2</sup> ster. is given (2) by the well known equation

$$I_m = (10^{-7}/4\pi) N_m L h \nu_0 A_t [g_u/B(T)] e^{-E_u/kT}, \quad [7]$$

where  $N_m$  is the minimum detectable number of atoms/cm.<sup>3</sup> of flame gases,  $h$  is Planck's constant in ergs/sec., the  $10^{-7}$  is necessary to convert from ergs/sec. to watts,  $\nu_0$  is the frequency of maximum intensity of the spectral line in sec.<sup>-1</sup>,  $A_t$  is the transition probability in sec.<sup>-1</sup> for the transition from the upper state  $u$  to a lower state (usually the ground state of the atom, designated  $o$ ),  $E_u$  is the energy of the upper state,  $k$  is the Boltzmann constant in units consistent with  $E_u$ ,  $T$  is the absolute temperature, and  $L$  is the average diameter in cm. of the flame region being focused on the monochromator entrance slit.

The statistical weight of the upper state is  $g_u$ , and the partition function over all states is  $B(T)$ , which is defined by

$$B(T) = g_o + g_1 e^{-E_1/kT} + g_2 e^{-E_2/kT} \dots = \sum_i g_i e^{-E_i/kT}, \quad [8]$$

where the summation is carried out over all states. However, only in cases in which there are excited states within 1.5 to 2 e.v. of the



ground state (e.g., Cr at 3000°K in which  $B(T)$  is about 9 per cent greater than  $g_0$ ) does  $B(T)$  differ significantly from  $g_0$  and so in most cases the simplification  $B(T) = g_0$  can be made with negligible error. More correctly,  $N_m$  in equation [7] should be replaced by  $N_m^0$ , the ground state atomic concentration at the limit of detectability. The minimum detectable concentration,  $N_m$ , is related to  $N_m^0$  by the expression  $N_m^0 = N_m g_0 / B(T)$ , where, as discussed above,  $B(T) \cong g_0$  for most cases in flame spectrometry.

As long as the spectral line is single, sharp, and isolated, the value of  $I_m$  is given by equation [7]. If radiation from more than one line of the same element is passed by the spectroscopic system, then  $I_m$  must contain additional terms for each line similar to the right hand term of equation [3]. In this case  $i_m$  will be given by an equation similar to equation [5], namely,

$$i_m = T_f W H (A/F^2) n \Sigma \kappa_j \gamma_j I_{mj} , \quad [9]$$

where the summation is over all spectral components passed by the exit slit. Since all components will not be passed centrally through the exit slit,  $\kappa_j$ , the slit function for each spectral component passed by the exit slit, will be less than unity for each line. The photosensitivity factor,  $\gamma_j$ , for each spectral line passed by the exit slit will, however, be nearly the same as the photosensitivity factor for the wavelength at which the monochromator is set as long as the change in  $\gamma$  with wavelength is small over the spectral slit width of the instrument. In any event it would be a relatively simple matter to determine the value of  $\gamma_j$  for each spectral line passed by the exit slit by means of

the manufacturer's spectral response curves for the photomultiplier tubes being used.

The evaluation of  $K_j$  for each spectral component can be performed by equation [6]. The greatest problem in evaluating the summation in equation [9] is in determination of the number of spectral components passed by the exit slit, i.e., as the slit width becomes wider more spectral lines will be passed, especially for such elements as the transition metals and the rare earth metals which have complex spectra. A special problem results if spectral lines have wavelengths near the extremes of the slit distribution.

If the spectral line is so broad that the intensity read by the instrument is not the total line intensity, then additional factors must be included in equation [9]. This problem has been considered by Winefordner (41) and Brodersen (9). However, most spectral lines produced by excitation of atoms in flames are quite narrow compared with the spectral slit width of most monochromators, and so additional correction factors are rarely required.

It is not possible to consider in a general way the case in which the spectral line is not resolved from lines of other elements because this would require a detailed knowledge of the matrix in which the analysis is to be performed. In the following discussion, the spectral line will be considered single, sharp, and isolated, and the monochromator wavelength will be assumed to be adjusted to the line center (i.e.,  $K = 1$ ). In this way the optimum slit width can be determined by minimization of the limit of detection equation,  $I_m$  will be given by equation [7], and  $i_m$  will be given by  $i_m = \gamma T_f I_m W H A / F^2$  ( $K = 1$  and  $n = 1$ ). As noted in the above discussion, there are cases in which the assumption

of a single, sharp, and isolated line is not valid. However, it should be pointed out that even if in a particular case a line does not meet the criteria of single, sharp, and isolated, it is still possible to obtain exact results by substitution of the proper values into the summation of equation [9]. More energetic sources such as arcs, sparks, etc., certainly do not meet the above criteria.

The root-mean-square fluctuation current,  $\overline{\Delta i_T}$ , is a result of the root-mean-square fluctuation current due to noise in the flame source,  $\overline{\Delta i_c}$ , and the root-mean-square fluctuation current due to noise in the phototube,  $\overline{\Delta i_p}$ . The flame noise is primarily due to fluctuation in the intensity of the continuous background radiation, and the photodetector noise is due to the shot effect and thermal noise. The two noise signals add quadratically (19) so that  $\overline{\Delta i_T}$  is given by

$$\overline{\Delta i_T} = (\overline{\Delta i_p}^2 + \overline{\Delta i_c}^2)^{1/2}. \quad [10]$$

The value of  $\overline{\Delta i_p}$  is given (35) by

$$\overline{\Delta i_p} = (2e_c \Delta f B M (i_d + i_c) + 4kT_0 \Delta f / R_0)^{1/2}, \quad [11]$$

where  $e_c$  is the electronic charge in coulombs,  $B$  is a constant approximately equal to  $1 + 1/G + 1/G^2 + 1/G^3 + \dots$  where  $G$  is the gain per stage of the photomultiplier tube,  $M$  is the total amplification factor of the phototube, and  $\Delta f$  is the frequency response bandwidth in  $\text{sec.}^{-1}$  of the amplifier-readout circuit. Both flame noise and phototube noise are assumed to be equally distributed over  $\Delta f$ , i.e., the noise is assumed to be white (19). The dark current in amperes at the anode, produced by thermionic emission, is  $i_d$ , and the signal in amperes produced at the anode due to the incident intensity of continuous radiation



from the flame is  $i_c$ . The temperature of the load resistor in  $^{\circ}\text{K}$  is  $T_o$ , and the load resistor of the detector circuit has a resistance of  $R_o$  ohms.

The value of  $i_c$  in amperes is given (see Appendix A) by

$$i_c = Y T_f I_c W H (A/F^2) s , \quad [12]$$

where  $I_c$  is the intensity per unit wavelength interval of the continuum, i.e.,  $I_c$  has units of watts/cm.<sup>2</sup> ster. mp (called steradiancy per unit wavelength interval). The value of  $\overline{\Delta i_c}$  can also be shown to be given (see Appendix A) by

$$\overline{\Delta i_c} = Y T_f \overline{\Delta I_c} W H (A/F^2) s (\Delta f)^{1/2} , \quad [13]$$

where  $\overline{\Delta I_c}$  is the root-mean-square fluctuation in the intensity (or steradiancy) per unit wavelength interval of the continuum.

Combining several of the previous equations and solving for  $N_m$ , one may write

$$N_m = \frac{8\pi \cdot 10^7 B(T) e^{E_u/kT}}{h Y T_f W H (A/F^2) V_{og_u} A_t L} \overline{\Delta i_T} . \quad [14]$$

The equation for  $\overline{\Delta i_p}$  can be somewhat simplified because the thermal noise is generally (35) negligible when compared to the shot effect for most systems and so equation [11] becomes

$$\overline{\Delta i_p} = [2e_c B M \Delta f (i_d + i_c)]^{1/2} . \quad [15]$$

Substituting for  $\overline{\Delta i_p}$ ,  $i_c$  and  $\overline{\Delta i_c}$  and collecting terms, the expression for the minimum detectable concentration is obtained

$$N_m = \quad [16]$$

$$\frac{3.8 \times 10^{34} B(T) e^{E_u/kT} (2e_c B M \Delta f [I_d + \gamma_{T_f} I_c W H(A/F^2) s] + [\gamma_{T_f} \overline{\Delta I_c} W H(A/F^2) s]^2 \Delta f)^{1/2}}{V_o g_u A_t L \gamma_{T_f} W H A / F^2},$$

in units of atoms/cm.<sup>3</sup> of flame gases. The constant  $3.8 \times 10^{34}$  results when  $8\pi \times 10^7$  is divided by Planck's constant.

If  $N_m$  in equation [16] is differentiated with respect to  $W$  and minimized, then the condition for optimum slit width in cm.,  $W_o$ , is found to be satisfied when

$$[\gamma_{T_f} H(A/F^2) \overline{\Delta I_c} R_d]^2 W_o^4 + [\gamma_{T_f} H(A/F^2) \overline{\Delta I_c}]^2 s_c R_d W_o^3 - e_c B M \gamma_{T_f} H(A/F^2) I_c s_c W_o - 2e_c B M I_d = 0. \quad [17]$$

By evaluating all factors in equation [17] for the particular experimental setup in concern,  $W_o$  can be found. (Use of a graphical method is the simplest means.) If the flame background is low at the wavelength setting of the monochromator, then  $s_m$  is much larger than  $s_c$ , and  $s = s_m = R_d W$ . For this case  $W_o$  is given by an expression considerably simpler than equation [17], namely,

$$W_o = \left( \frac{2e_c B M I_d}{[\gamma_{T_f} \overline{\Delta I_c} H(A/F^2) R_d]^2} \right)^{1/4}, \quad [18]$$

where equation [18] can be found directly from equation [17] by assuming  $s_c$  is very small so that the second and third terms become negligible. As  $I_c$  and  $\overline{\Delta I_c}$  increase ( $\overline{\Delta I_c}$  increases approximately proportionally with  $I_c$  (17)), the last term in equation [17] becomes negligible when compared to the other terms. Therefore, at large values of  $I_c$ , the optimum slit width,  $W_o$ , decreases indefinitely and approaches zero.

The use of concentrations in atoms per  $\text{cm}^3$  of flame gases would have little meaning to most chemists. It would be more convenient to use concentrations in moles per liter of solution introduced into the given flame. If the concentration of sample is  $C$  moles per liter and if the sample is introduced into a given flame at a rate of  $\phi \text{ cm}^3/\text{min.}$  or  $\phi/60 \text{ cm}^3/\text{sec.}$ , then  $\phi/60 \times 1000$  liters or  $C\phi/60 \times 1000$  moles of sample are introduced each second. The number of atoms per second introduced into the flame is then  $C\phi \times 10^{23}/60 \times 1000$ . If  $Q$  is the flow rate of unburned gases in  $\text{cm}^3/\text{sec.}$  introduced at room temperature and one atmosphere pressure, then  $C\phi \times 10^{23}/60 \times 10^3 Q$  is the number of atoms per  $\text{cm}^3$  of flame gases.

This expression assumes thorough mixing of the sample with the flame gases, no entrainment of atmosphere, no expansion of burnt gases, 100 per cent efficiency of sample introduction (42), and complete dissociation of the salt crystals into atoms. With a total consumption atomizer-burner nearly complete mixing of sample with flame gases occurs in the outer cone of the flame. No detailed equations can be given to consider the extent of atmosphere entrainment because it depends on the exact experimental arrangement. The expansion of burnt gases has been accounted for by Alkemade (1) by use of an expansion factor  $e_f$ . Winefordner, Mansfield, and Vickers (42) have accounted for incomplete dispersion of sample solution into droplets and incomplete solvent evaporation by use of a sample introduction efficiency factor  $\epsilon$ . A factor  $\beta$  will be used to account for incomplete dissociation of salt crystals into atoms and atomic losses due to ionization and compound formation with flame product gases. Therefore, using  $e_f$ ,  $\epsilon$ , and  $\beta$  in

the previous equation, the flame gas concentration  $N$  in atoms per cm.<sup>3</sup> of flame gases can be converted to solution concentration  $C$  in moles per liter by

$$C = \frac{6 \times 10^4 \cdot e_f Q N}{6 \times 10^{23} \phi \epsilon \beta} \quad [19]$$

The term  $e_f$  has been evaluated by Alkemade (1) and is given by

$$e_f = n_T T / n_{298} 298, \quad [20]$$

where  $T$  is the flame temperature in  $^{\circ}\text{K}$ ,  $n_T$  is the number of moles of combustion products at temperature  $T$  and  $n_{298}$  is the number of moles of species at room temperature, which is taken as  $298^{\circ}\text{K}$ . in this case. Thus the final form of the conversion equation is given by

$$C = 3.3 \times 10^{-22} \frac{n_T Q T N}{n_{298} \phi \epsilon \beta}, \text{ moles/liter.} \quad [21]$$

In the above equation, the values of  $n_T$  and  $n_{298}$  must include not only the moles of flame gas products due to the fuel combining with oxygen but also the moles due to the vaporization of the solvent introduced. Equation [21] can be used to calculate the minimum detectable solution concentration of a given atomic species once the minimum detectable concentration of atoms in the flame has been calculated.

### Discussion and Calculations

Equation [16] for  $N_m$  is a general expression and should allow the accurate calculation of limiting detectable concentrations for any

element, present in any given flame, and analyzed using any given experimental setup, as long as accurate data are available to evaluate the factors. In many cases good data will not be available, and this will prevent accurate absolute values of  $N_m$  from being calculated. However, it should be stressed that the usefulness of equation [16] lies not only in the calculation of detection limits but also in the prediction of the effect of changing various experimental factors on the limit of detection. In addition, if sufficiently accurate data are available, then it should be possible to determine accurate transition probabilities if accurate measurements of absolute intensities are made.

It should be noted that equation [16] for  $N_m$  is exact as long as the spectral line is single, sharp, and isolated, and if this is not the case, then the other spectral lines passed through the exit slit must be corrected for in the manner discussed in the preceding portion of the paper. Also the equations derived should apply whether single stage phototubes or multistage phototubes (photomultipliers) are used as detectors.

The use of equation [17] for calculating  $W_0$  and equation [16] for calculating  $N_m$  is illustrated by the representative results in Table 1 for Na 5890 A. and Cd 2288 A. lines analyzed using the experimental conditions and data listed at the end of Table 1. However, equation [18] gives essentially the same value of  $W_0$  as equation [17] because of the low flame background.

The values of  $F$ ,  $A$ ,  $T_f$ ,  $H$ , and  $R_d$  listed in Table 1 were representative values taken from the manufacturer's literature. Photomultiplier tube characteristics vary with individual tubes and for



accurate work  $i_d$ ,  $M$ , and  $\gamma$  must be experimentally measured for the particular detector. For the purpose of this paper the value of  $i_d$  given by the manufacturer for a good 1P28 photomultiplier has been taken. Because the amplification factor,  $M$ , is related to the anodic photosensitivity,  $\gamma$ , by a constant characteristic of the photocathodic surface and because the anodic dark current  $i_d$  equals  $M$  times the cathodic dark current, the value of  $N_m$  is independent of  $M$  and  $\gamma$ . However, characteristics of phototubes are generally reported in terms of anodic rather than cathodic output, and therefore, anodic dark current and anodic photosensitivity are used in the theory of this manuscript. The values of  $M$  and  $\gamma$  given in the manufacturer's literature have been taken as typical. The values of  $\gamma$  at the wavelengths of interest were corrected for variation in spectral response from the manufacturer's response curves. The gain,  $G$ , per stage of a photomultiplier tube is of the order of 4, and so the value of  $B$  is taken as 1.3.

The absolute background intensities,  $I_c$  for oxyhydrogen and oxyacetylene flames in units of  $\text{watts/cm}^2 \text{ ster. mu}$  have been taken from the plots of  $I_c$  versus wavelength given by Gilbert (17). Gilbert also gives similar plots for air-hydrogen and air-acetylene flames. The value of  $\overline{\Delta I_c}$  is given by  $\xi I_c$ , where  $\xi$  is the ratio of the root-mean-square fluctuation in the background intensity to the value of the background intensity. The value of  $\xi$  depends upon the temperature fluctuations, irregularities of atomization at the spray tip, mechanical turbulence in the spray and the burning gases, and turbulence due to friction and mixing with the ambient air (17,20). Of these factors only



TABLE 1

REPRESENTATIVE RESULTS IN ATOMIC EMISSION FLAME SPECTROMETRY FOR LIMITS OF DETECTABILITY IN NUMBER OF ATOMS PER CM.<sup>3</sup> OF FLAME GASES FOR TWO ELEMENTS (Na AND Cd) IN TWO FLAMES AND FOR TWO MONOCHROMATORS WITH OPTIMUM SLIT WIDTHS<sup>a</sup>

| Monochromator  | Beckman DU Quartz Prism <sup>b</sup>             |                                                                              | Jarrell-Ash 500 mm. Ebert Grating <sup>c</sup>                |                                                                              |
|----------------|--------------------------------------------------|------------------------------------------------------------------------------|---------------------------------------------------------------|------------------------------------------------------------------------------|
|                | Stoichiometric<br>H <sub>2</sub> /O <sub>2</sub> | Stoichiometric <sup>e</sup><br>C <sub>2</sub> H <sub>2</sub> /O <sub>2</sub> | Stoichiometric <sup>e</sup><br>H <sub>2</sub> /O <sub>2</sub> | Stoichiometric <sup>e</sup><br>C <sub>2</sub> H <sub>2</sub> /O <sub>2</sub> |
| Flame Type     | W <sub>O</sub> , cm. N <sub>m</sub>              | W <sub>O</sub> , cm. N <sub>m</sub>                                          | W <sub>O</sub> , cm. N <sub>m</sub>                           | W <sub>O</sub> , cm. N <sub>m</sub>                                          |
| Na 5890 A. d,f | 0.016 7.7 x 10 <sup>5</sup>                      | 0.006 1.8 x 10 <sup>6</sup>                                                  | 0.074 1.6 x 10 <sup>5</sup>                                   | 0.028 1.3 x 10 <sup>5</sup>                                                  |
| Cd 2288 A. d,f | 0.051 1.0 x 10 <sup>11</sup>                     | 0.021 3.8 x 10 <sup>10</sup>                                                 | 0.046 1.1 x 10 <sup>11</sup>                                  | 0.019 4.2 x 10 <sup>10</sup>                                                 |

## Atomic Line

<sup>a</sup>All calculation of N<sub>m</sub> were made using equation [16], and W<sub>O</sub> calculations were made using equation [17].

<sup>b</sup>F = 50 cm., A = 25 cm.<sup>2</sup>, T<sub>f</sub> = 0.5, H = 1.0 cm., R<sub>d</sub> = 303 mm/cm. at 5890 A. and 13 mm/cm. at 2288 A.

<sup>c</sup>F = 50 cm., A = 27 cm.<sup>2</sup>, T<sub>f</sub> = 0.5, H = 1.0 cm., R<sub>d</sub> = 16 mm/cm. at 5890 A. and at 2288 A.

<sup>d</sup>Assuming a good 1P28 photomultiplier tube is used for the calculations in the table, then i<sub>d</sub> = 10<sup>-7</sup> amp., M = 10<sup>6</sup>, B = 1.3, Y = 1 x 10<sup>4</sup> at 5890 A. and Y = 2 x 10<sup>4</sup> at 2288 A. The value of Δf is taken as 1 sec.<sup>-1</sup>.

<sup>e</sup>For a stoichiometric H<sub>2</sub>/O<sub>2</sub> flame in which aqueous solution is introduced at 2 cm.<sup>3</sup>/min., the flame temperature, T, is taken as 2700°K., and the flame diameter, L, as 0.5 cm. The value of I<sub>c</sub> (17) at 5890 A. is taken as 1.0 x 10<sup>-8</sup> watt/cm.<sup>2</sup> ster. mm, and at 2288 A. is taken as 1.3 x 10<sup>-8</sup> watts/cm.<sup>2</sup> ster. mm.

For a stoichiometric C<sub>2</sub>H<sub>2</sub>/O<sub>2</sub> flame in which aqueous solution is introduced at 2 cm.<sup>3</sup>/min. the flame temperature, T, is taken as 2850°K. and the flame diameter, L, as 1.0 cm. The value of I<sub>c</sub> (17) at 5890 A. is taken as 7 x 10<sup>-8</sup> watt/cm.<sup>2</sup> ster. mm, and at 2288 A. is taken as 8 x 10<sup>-8</sup> watt/cm.<sup>2</sup> ster. mm.

The r.m.s. flicker of both flames in good adjustment will be taken as 0.005 and so ΔI<sub>c</sub> = 0.005I<sub>c</sub>.

<sup>f</sup>For the Na 5890 A. line, A<sub>t</sub> = 1.3 x 10<sup>8</sup> sec.<sup>-1</sup>, g<sub>u</sub> = 4, B(T) = g<sub>o</sub> = 2, E<sub>u</sub> = 2.10 e.v. For the Cd 2288 A. line, A<sub>t</sub> = 1.7 x 10<sup>8</sup> sec.<sup>-1</sup>, g<sub>u</sub> = 3, B(T) = g<sub>o</sub> = 1, E<sub>u</sub> = 5.4 e.v. (28).

the fluctuation due to temperature variation can be readily represented by an expression. The background intensity of the continuum varies approximately as  $\exp(-h\nu/kT)$  and so an approximate value of  $\xi$  can be found by differentiating  $I_c$  with respect to  $T$  to find the relationship between  $\xi$  and  $\overline{\Delta T}$ , the root-mean-square temperature fluctuation. If this is done,  $\xi$  is found (1) to be given by  $(h\nu/k) (\overline{\Delta T}/T^2)$ , which will be smaller than the true  $\xi$  due to neglect of the other factors mentioned above. A Beckman flame in good adjustment (at 3000°K. and 5000 Å.) results in a value of  $\xi$  of approximately 0.005. If only temperature variation is considered, this value of  $\xi$  will result from a temperature fluctuation of about 2°K. The use of a sheathed burner as described by Gilbert (18) allows even better stability. Experimental values of  $\xi$  can be measured by finding the magnitude of the peak-to-peak noise as compared to the value of the background signal and multiplying by  $\sqrt{2}/4$  to convert to r.m.s. noise (19).

By the use of equation [21], the  $N_m$  values in Table 1 can be converted to more meaningful solution concentrations in moles/liter. For a typical oxyacetylene flame with a temperature of 2850°K. at 1 cm. above the inner cone (43), when an aqueous solution is introduced into the flame via a total-consumption atomizer-burner, at a flow rate of 2 cm.<sup>3</sup>/min., a concentration of  $1.8 \times 10^6$  atoms of Na per cm.<sup>3</sup> of flame gases was found to be equivalent to a solution concentration of  $1.6 \times 10^{-4}$  p.p.m. This value agrees quite well with the value given by Gilbert (17).

In this calculation the flow rates of C<sub>2</sub>H<sub>2</sub> and O<sub>2</sub> were, respectively, taken as 2500 cm.<sup>3</sup>/min. and 3750 cm.<sup>3</sup>/min. This would result

in a value of  $Q$  of  $125 \text{ cm}^3/\text{sec}$ . if allowance is made for the sample vapor, assuming that the sample vapor is not appreciably dissociated (46). The data for  $n_T$  and  $n_{298}$  were taken from the thesis by Zaer (46). The ratio  $n_T/n_{298}$  is approximately 1.2. The efficiency of atomization was taken as approximately 0.5 according to data by Winefordner, Mansfield, and Vickers (42).

The value of  $\beta$  was determined primarily by ionization of sodium atoms, although the formation of  $\text{NaOH}$  in the flame (16,24) may cause  $\beta$  to be slightly less than by ionization alone. An approximate value of  $\beta$  was determined in the following way. The ionization constant for the process  $\text{Na} \rightarrow \text{Na}^+ + e^-$  was calculated to be  $1.01 \times 10^{-7} \text{ atm}$ . at  $2850^\circ\text{K}$ . from the expression given by Mavrodineanu and Boiteux (30). The partial pressure of electrons due only to the flame gases was taken as approximately  $4 \times 10^{-9} \text{ atm}$ . (15) in the outer cone of a  $\text{C}_2\text{H}_2/\text{O}_2$  flame at  $2850^\circ\text{K}$ . This partial pressure of free electrons corresponds to  $10^{10}$  electrons per  $\text{cm}^3$  of flame gases assuming the flame gas solution of free electrons is an ideal gas. Using the above data, the degree of ionization was found to be 0.96 and, therefore,  $\beta$  was found to be 0.04. The degree of ionization calculated agrees quite well with values calculated by Gaydon and Wolfhard (15) and Foster (12) for the outer cone of acetylene flames.

The above calculation did not account for additional dilution of the analyte vapor due to entrainment of ambient air. Except under accurately controlled conditions, this additional effect is not determinable. If this effect is accurately known, then  $Q$  and  $n_T/n_{298}$  should be correspondingly corrected. However, this is unnecessary unless the

most accurate possible results are needed, such as when the described theory is applied to the calculation of transition probabilities for unknown cases. If this is done, it is best to use well defined, sheathed, homogeneous flames in order that  $N_m$  is accurately known.

In Table 2 the effect of flame temperature on  $W_0$  and  $N_m$  is given for the resonance lines of Na and Cd when analyzed by a Beckman DU monochromator 1P28 photomultiplier detector combination. The resonance lines of Na and Cd differ quite greatly in wavelength and in excitation energy and were especially chosen to illustrate the influence of excitation energy on the limit of detectability as a function of several flame temperatures. No single flame type can be used to cover the broad range of flame temperatures listed in Table 2 (see item 2 at end of table), and so the flame type is not specified. However, a stoichiometric air-acetylene flame has approximately a temperature of 2000°K., a stoichiometric oxyacetylene flame has approximately a temperature of 3000°K., and an oxycyanogen flame has approximately a temperature of 4000°K. when aqueous solutions are introduced from total consumption atomizer-burners at the rate of about 1 cm.<sup>3</sup>/min. The values of  $I_c$  listed in Table 2 were considered typical and should not be considered as accurate values for the above flames.

As can be noted from Table 2, an increase in flame temperature results in an improvement in limit of detectability and a decrease in optimum slit width. With elements having their resonance lines in the u.v., an increase in flame temperature gives a great increase in sensitivity as a result of the exponential factor in equation [16]. However, for elements with their resonance lines in the visible the increase



TABIE 2

CALCULATED VALUES OF OPTIMUM SLIT WIDTHS<sup>a</sup> IN CM. AND LIMIT OF DETECTABILITY<sup>a</sup> IN ATOMS PER CM.<sup>3</sup>  
FOR SEVERAL ELEMENTS WITH RESONANCE LINES IN WIDELY DIFFERENT SPECTRAL REGIONS AS A  
FUNCTION OF FLAME TEMPERATURE<sup>b</sup> FOR A REPRESENTATIVE MONOCHROMATOR-DETECTOR<sup>c</sup> SETUP

| Atomic Line  | Temperature<br>OK. |                      | 2000  |                      | 3000  |                   | 4000  |       |
|--------------|--------------------|----------------------|-------|----------------------|-------|-------------------|-------|-------|
|              | $W_0$              | $N_m$                | $W_0$ | $N_m$                | $W_0$ | $N_m$             | $W_0$ | $N_m$ |
| Na 5890 A. d | 0.17               | $7.6 \times 10^6$    | 0.008 | $7.8 \times 10^5$    | 0.005 | $4.8 \times 10^5$ |       |       |
| Cd 2288 A. d | 0.20e              | $9.2 \times 10^{13}$ | 0.021 | $2.1 \times 10^{11}$ | 0.009 | $5.4 \times 10^8$ |       |       |

<sup>a</sup>All calculations of  $N_m$  and  $W_0$  were done using equations [16] and [17], respectively.

<sup>b</sup>Because no single flame type is likely to cover the large range of temperatures from 2000 to 4000°K., no flame type will be listed. The above table is used only to show the great influence of flame temperature on the value of  $N_m$ . Because no flame type is specified, the values of  $I_c$  at 2288 Å. will be taken as  $10^{-10}$ ,  $10^{-7}$ , and  $10^{-6}$  watts/cm.<sup>2</sup> ster. mp at 2000, 3000, and 4000°K., respectively. The values of  $I_c$  at 5890 Å. will be taken as  $10^{-9}$ ,  $10^{-7}$ , and  $10^{-6}$  watts/cm.<sup>2</sup> ster. mp at 2000, 3000, and 4000°K., respectively.

<sup>c</sup>Assuming a Beckman DU Quartz Prism Monochromator with 1P28 photomultiplier detector is used, the values of F, A, T, H,  $R_d$ ,  $i_d$ , M, B, and  $\gamma$  will be the same as those listed in items b and d at the end of Table 1.

<sup>d</sup>The values of  $A_t$ ,  $E_u$ ,  $g_u$ , and  $g_0$  will be the same as listed in item e at the end of Table 1. The value of L will be taken as 1.0 cm.

<sup>e</sup>In this case  $W_0$  was found to be 0.58 cm., but since the mechanical limit of the slit on the Beckman DU is 0.2 cm., the value of 0.2 cm. was used to calculate  $N_m$ .

in sensitivity, i.e., decrease in value of  $N_m$ , with flame temperature is not as great as might be expected. This neglects any adverse effects due to ionization and is due only to the increase in  $I_c$  and  $\overline{\Delta I_c}$  associated with an increase in flame temperature and a smaller increase in the exponential factor of equation [16]. Therefore, for elements with spectral lines in the visible, no significant advantage may result by the use of higher temperature flames, e.g., oxycyanogen or fluorine-hydrogen, rather than the usual flames of oxyhydrogen or oxyacetylene (or even air-acetylene), and in some cases an exceptionally high background may result in a decreased sensitivity. The data used to obtain the results given in Table 2 are listed at the end of the table.

The shape of the  $N_m$  versus slit width,  $W$ , curve for any particular experimental setup and spectral line should be of special interest to the analyst. If this curve has a broad flat minimum, then the exact setting of the slit width for optimum conditions is not critical. Because the shape of the  $N_m$  versus  $W$  function is independent of the spectral line, it is not necessary to evaluate all factors in equation [16] at a variety of slit widths, but rather it is possible to combine all factors except  $1/W$  outside the square root sign into a constant factor designated  $K_c$ . This constant  $K_c$  is a function of the particular line, flame and instrumental setup but is independent of  $W$ . Therefore, by replacing  $s$  by  $R_d W$  and evaluating all universal constants, equation [16] can be rewritten as

$$N_m = \quad [22]$$

$$(K_c/W) (5 \times 10^{-19} M [i_d + \gamma T_f I_c H(A/F^2) R_d W^2] + [\gamma T_f \overline{\Delta I_c} H(A/F^2) R_d]^2 W^4)^{1/2}$$



where all factors within the square root must be evaluated for the particular experimental conditions. It is evident from the above equation that the shape of  $N_m$  as a function of  $W$  is not dependent on the magnitude of  $K_c$ . In Table 3 values of  $N_m$  have been calculated from equation [22] for various  $W$  values, and, as expected, the minimum value of  $N_m$  occurs at  $W_0$ .

As can be seen from the results in Table 3,  $N_m$  varies approximately linearly with  $W$  for large  $W$  values and  $1/W$  for small  $W$  values. The particular experimental conditions for which the calculations were made are given at the end of the table. For the experimental conditions listed in Table 3, the  $N_m$  versus  $W$  curve has quite a flat minimum. In fact the value of  $W$  can deviate from  $W_0$  by a factor of 2, and  $N_m$  increases by a factor of no more than 1.4.

The above discussion regarding equation [22] is valid only if the spectral line is resolved as a single, sharp line. If two or more spectral lines are collected by the exit slit, then equation [22] must be modified accordingly, as previously discussed. In the latter case, a plot of  $N_m$  versus  $W$  may result in more than one minimum of  $N_m$  for certain optimal wavelength settings. For example, with hydrogen flames and prism monochromators, the most sensitive spectral line of elements such as Fe, Co, Ni, Ru, Rh, and Cr are not fully separated. Even the best prism monochromator with the narrowest useable slits may not be able to isolate the sensitive lines of the rare earths.

Several other cases will be given which demonstrate the effect of various factors on the optimum slit width. A small value of  $W_0$  ( $W_0 = 0.002$  cm.) results when using equation [18] for the following

TABLE 3

VARIATION OF  $N_m$  WITH  $W$  FOR A PRISM MONOCHROMATOR AT 420 mμ WHEN  
USING AN OXYHYDROGEN FLAME\*

| $W$ , cm.       | $N_m$                     |
|-----------------|---------------------------|
| 0.001           | $7.1 \times 10^{-8} K_c$  |
| 0.005           | $1.5 \times 10^{-8} K_c$  |
| 0.008           | $1.0 \times 10^{-8} K_c$  |
| 0.010           | $0.90 \times 10^{-8} K_c$ |
| 0.012           | $0.82 \times 10^{-8} K_c$ |
| 0.015 ( $W_o$ ) | $0.78 \times 10^{-8} K_c$ |
| 0.020           | $0.79 \times 10^{-8} K_c$ |
| 0.030           | $0.91 \times 10^{-8} K_c$ |
| 0.050           | $1.3 \times 10^{-8} K_c$  |
| 0.100           | $2.6 \times 10^{-8} K_c$  |

\*The above calculations were performed using equation [22] and the following data:  $i_d = 10^{-8}$  amp. (for a good 1P28 photomultiplier tube),  $\gamma = 10^4$  amp./watt,  $M = 10^6$ ,  $T_f = 0.5$ ,  $H = 1$  cm.,  $A = 25$  cm.<sup>2</sup>,  $F = 50$  cm.,  $R_d = 100$  mμ/cm.,  $\Delta f = 1$  sec.<sup>-1</sup>, and  $\Delta I_c = 5 \times 10^{-11}$  watts/cm.<sup>2</sup> ster. mμ sec.<sup>-1/2</sup>.

Using the above data and equation [18],  $W_o$  is 0.015 cm.

conditions:  $i_d = 10^{-8}$  amperes (a good 1P28),  $\gamma = 10^4$  (a good 1P28 at 400 mμ),  $B = 1.3$ ,  $M = 10^6$ ,  $T_f = 0.5$ ,  $R_d = 100$  mμ/cm. (for a prism monochromator at 400 mμ),  $\overline{\Delta I_c} = 3 \times 10^{-9}$  for an oxyacetylene flame at 400 mμ, and  $HA/F^2 = 0.01$ . For this case the value of  $W_o$  is of the same order as the practical (effective) resolving power expressed in terms of slit width. In the Beckman DU monochromator, the practical resolving power slit width (20) is about 0.003 cm. in the visible and 0.006 cm. at the shortest useable wavelengths, and it is determined by the combination of diffraction, coma, aberrations, slit curvature mismatch, and optical imperfections. Therefore, for this particular case, the limit of detectability will be considerably lowered if the slit width is made smaller than the effective resolving power slit width although no gain in resolution will occur. If in the above case the values of  $I_c$  and  $\overline{\Delta I_c}$  are increased by  $10^3$  corresponding to a brilliant background in a plasma flame,  $W_o$  is approximately 0.00007 cm., which is considerably less than the effective resolving power slit width.

A case in which a wide slit width value of  $W_o$  results would be the case in which  $i_d = 3 \times 10^{-8}$  (maximal specification for a 16PMI photomultiplier tube),  $\gamma = 10^2$  (at 630 mμ),  $B = 1.3$ ,  $M = 10^5$ ,  $T_f = 0.2$  (for a grating monochromator),  $R_d = 10$  mμ/cm.,  $HA/F^2 = 0.005$ , and  $\overline{\Delta I_c} = 3 \times 10^{-12}$  watts/cm.<sup>2</sup> ster. mμ sec.<sup>-1/2</sup> (a good stable H<sub>2</sub>/air flame at 630 mμ). For this case  $W_o = 3.4$  cm., which is a very wide slit. Assuming no lines are present other than the line of interest, it is interesting to find how much sensitivity is lost if a narrower slit is used. From equation [22],  $N_m$  is 1.4 times greater at  $W = 1.6$  cm. than at  $W = 3.4$  cm. and is 4 times greater at  $W = 0.5$  cm. than at  $W = 3.4$  cm.

In this case the value of  $W_0$  found by using equation [18] is so large that it is essentially the same as that given by equation [17].

### III. CALCULATION OF THE LIMIT OF DETECTABILITY FOR ATOMIC ABSORPTION FLAME SPECTROMETRY

#### Introduction

The system under consideration in the development of this theory consists of a hollow cathode discharge tube (HCDT), or other resonance lamp which emits sufficiently narrow lines, a flame into which the sample is aspirated, a lens for focusing radiation from the source onto the central part of the outer cone of the flame (which can be considered to be approximately in thermal equilibrium), a second lens for focusing the transmitted radiation onto the monochromator entrance slit, a monochromator with accompanying optics and slits, a photodetector, amplifier, and readout (recorder, meter, etc.). The HCDT emits a line of intensity  $I^0$  (in watts/cm.<sup>2</sup> ster.), and the intensity of the transmitted radiation is  $I_t$  (in the same units as  $I^0$ ). The transmitted radiation is focused by the second lens onto the entrance slit of the monochromator so that the slit is fully illuminated and the effective aperture of the spectrometric system is filled with radiation.

It is assumed that correction is made for thermally emitted and fluorescent radiation of the same frequency as the incident radiation so that  $I_t$  is the true transmitted intensity, i.e., it does not include emission from the flame other than flame noise in the frequency interval,  $\Delta f$ , over which the amplification-readout system responds. Also it is assumed that correction is made for any radiation loss due to scattering by droplets in the flame. Further it is assumed that the monochromator



is set on the line center,  $\nu_0$  (the frequency of the absorption line peak in  $\text{sec.}^{-1}$ ), and that only radiation of the line of interest enters the spectrometric system.

### Derivation of Equations

If the spectral line emitted by the source is much narrower than the absorption lines in the flame, then  $I^0$  is related to  $I_t$  by Beer's Law

$$A^0 = \log (I^0/I_t) = 0.43k^0L, \quad [23]$$

where  $A^0$  is the absorbance,  $k^0$  is the atomic absorption coefficient in  $\text{cm.}^{-1}$  at the line center for any atomic concentration, and  $L$  is the length in cm. of flame gases through which the radiation is passed. Justification for the assumption of a narrow source line is to be found in the statements of Jones and Walsh (26) and Crosswhite (11) and in the ability of the experimenter to adjust the source line width by changing the operating current of the tube, or, if necessary, even by cooling the tube. (However, see Appendix C for a further discussion of the effect of line width.)

Thus it is seldom necessary to operate under conditions in which the effect of Doppler, Lorentz, and Holtsmark line broadening is more important in the source than in the flame. However, it may occur that a line is intrinsically broad due to hyperfine structure, both from nuclear spin effect and isotope shift. It may be shown (see Appendix D) that the effect of hyperfine structure is to reduce the absorbance below the expected value. Thus

$$A^0 = \log (I^0/I_t) = 0.43\rho k^0 L , \quad [24]$$

where  $\rho$  is the correction factor to account for the decrease in absorbance. The method of calculating  $\rho$  is indicated in Appendix D.

The absorbance will be said to be just detectable when the difference between the detector output signal (anodic current of the photodetector)  $i^0$ , in amperes, due to  $I^0$  and the detector output signal  $i_t$ , in amperes, due to  $I_t$  equals twice the total root-mean-square noise fluctuation. It is assumed in this theory that the noise is measured at the wavelength of the line of interest with solvent aspirated into the flame.

Thus the minimum detectable signal difference is given by

$$(i^0 - i_t)_m = 2\overline{\Delta i_T} , \quad [25]$$

where  $\overline{\Delta i_T}$  is the total root-mean-square noise fluctuation in the output current of the photodetector in amperes, and the subscript m indicates that the signal difference is that observed at the minimum detectable concentration. The relationship between signal in amperes and intensity in watts/cm.<sup>2</sup> ster. has been derived in Appendix A. Thus it may be shown that

$$i^0 = \gamma T_f W H (A/F^2) I^0 , \quad [26]$$

and

$$i_t = \gamma T_f W H (A/F^2) I_t , \quad [27]$$

where all the terms have been previously defined.

Substituting for  $i^0$  and  $i_t$  in equation [25] one obtains

$$\gamma_{T_f WH(A/F^2)} (I^0 - I_t)_m = 2\overline{\Delta i_T} . \quad [28]$$

However, from equation [24],  $I_t$  can be written in terms of  $I^0$  to obtain

$$\gamma_{T_f WH(A/F^2)} I^0 (1 - e^{-\rho k_m^0 L}) = 2\overline{\Delta i_T} , \quad [29]$$

where  $k_m^0$  is the atomic absorption coefficient at the line center at the minimum detectable concentration. Expanding the exponential term and noting that  $k_m^0 L$  is small at the limit of detection, i.e.,  $e^{-\rho k_m^0 L} = 1 - \rho k_m^0 L$ , one may write

$$\gamma_{T_f WH(A/F^2)} I^0 \rho k_m^0 L = 2\overline{\Delta i_T} , \quad [30]$$

The root-mean-square noise signal,  $\overline{\Delta i_T}$ , may be attributed to fluctuations originating in the photodetector,  $\overline{\Delta i_p}$ , fluctuations in the source,  $\overline{\Delta i^0}$ , and fluctuations in the flame continuum,  $\overline{\Delta i_c}$ . The noise signals add quadratically (18), and therefore,  $\overline{\Delta i_T}$  is given by

$$\overline{\Delta i_T} = (\overline{\Delta i_p}^2 + \overline{\Delta i^0}^2 + \overline{\Delta i_c}^2)^{1/2} . \quad [31]$$

The value of  $\overline{\Delta i_p}$  is given (35) by

$$\overline{\Delta i_p} = [2BMe_c \Delta f (i_d + i^0 + i_c)]^{1/2} , \quad [32]$$

where  $B$  is a constant approximately equal to  $1 + 1/G + 1/G^2 + \dots$ , where  $G$  is the gain per stage of the photodetector,  $M$  is the total amplification factor of the photodetector,  $e_c$  is the electronic charge in coulombs,  $i_d$  is the photodetector dark current in amperes, and  $i_c$  is the anodic current of the photodetector in amperes due to the continuous

emission of the flame. In any practical case in atomic absorption flame spectrometry  $i_d$  and  $i_c$  will be much smaller than  $i^0$  or, at least, can be made much smaller at the limit of detectability. Hence one may write

$$\overline{\Delta i_p} = (2BMe_c \Delta f i^0)^{1/2}, \quad [33]$$

and substituting from equation [26] one obtains for  $\overline{\Delta i_p}^2$

$$\overline{\Delta i_p}^2 = 2BMe_c \Delta f \gamma T_f WH (A/F^2) I^0. \quad [34]$$

The value of  $\overline{\Delta i^0}^2$  is related to the fluctuation in the intensity of incident radiation by

$$\overline{\Delta i^0}^2 = [\gamma T_f WH (A/F^2) \overline{\Delta I^0}]^2 \Delta f, \quad [35]$$

where  $\overline{\Delta I^0}$  is the fluctuation in the intensity of radiation from the source in units of watts/cm.<sup>2</sup> ster. sec.<sup>-1/2</sup>. The sec.<sup>-1/2</sup> unit arises because the noise is a root-mean-square noise. The relationship between the noise signal and the response bandwidth,  $\Delta f$ , in sec.<sup>-1</sup>, has been more fully discussed in Section II.

Similarly,  $\overline{\Delta i_c}$  is given by

$$\overline{\Delta i_c}^2 = [\gamma T_f WH (A/F^2) \overline{\Delta I_c} s]^2 \Delta f, \quad [36]$$

where  $\overline{\Delta I_c}$  is the fluctuation in the intensity of the continuum emitted by the flame in watts/cm.<sup>2</sup> ster. mp sec.<sup>-1/2</sup>, and  $s$  is the effective spectral slit width (in mp) of the spectrometric system.

The spectral slit width is given by the expression

$$s = (s_m^2 + s_c^2)^{1/2}, \quad [37]$$

where  $s_m$  is the spectral slit width in mp as determined by the mechanical

slit width, and  $s_c$  is the spectral slit width in  $m\mu$  at an infinitely narrow mechanical slit width as determined by diffraction and by coma, aberrations, mismatch of slit curvature, imperfection of optics, and other factors characteristic of an imperfect monochromator. Expression [37] differs from the one given for  $s$  in Section II since in the atomic absorption case, the more exact equation for  $s$  can be used without overly complicating the theory.

It will be convenient in calculating the noise terms to write the fluctuation as fractions of the total intensity such that  $\overline{\Delta I^0} = \chi I^0$  and  $\overline{\Delta I_c} = \xi I_c$ , where  $\chi$  and  $\xi$  are the appropriate fractions, and  $I_c$  is the intensity of the continuum emitted by the flame in units of  $\text{watts/cm}^2 \text{ ster. } m\mu$ . Equations [35] and [36] may then be rewritten in the following form:

$$\overline{\Delta i^0}^2 = [\gamma_{T_f W H (A/F^2)} \chi I^0]^2 \Delta f, \quad [38]$$

$$\overline{\Delta i_c}^2 = [\gamma_{T_f W H (A/F^2)} \xi I_c s]^2 \Delta f. \quad [39]$$

Substituting the appropriate values into equation [31], one obtains for  $\overline{\Delta i_T}$

$$\overline{\Delta i_T} = \left( [\gamma_{T_f W H (A/F^2)}]^2 \Delta f \left\{ \frac{2 B M e c I^0}{\gamma_{T_f W H A/F^2}} + (\chi I^0)^2 + (\xi I_c s)^2 \right\} \right)^{1/2}. \quad [40]$$

The value of  $k_m^0$ , the atomic absorption coefficient at the line center at the minimum detectable ground state concentration  $N_m^0$ , is given (31) by

$$k_m^0 = \frac{2 \sqrt{\ln 2} \lambda_0^2 g_u N_m^0 A_t \delta}{\Delta \nu_D \sqrt{\pi} 8 \pi g_o} = \frac{0.037 \lambda_0^2 g_u N_m^0 A_t \delta}{g_o \Delta \nu_D}, \quad [41]$$

where  $\Delta \nu_D$  is the Doppler half width (in  $\text{sec.}^{-1}$ ) of the absorption line,





$\lambda_0$  is the wavelength (in cm.) of the line center,  $g_u$  and  $g_o$  are the statistical weights of the upper u, state and the lower (ground, o) state,  $A_t$  is the transition probability in  $\text{sec.}^{-1}$  for spontaneous emission, i.e., state u to state o, and  $\mathcal{S}$  is a factor to account for line broadening other than Doppler broadening and hyperfine structure broadening (see Appendix D). Because analytically important atomic absorption transitions usually involve the ground state, only transitions to that state will be considered. The constants have been evaluated in the right hand part of equation [41].

The number of ground state atoms per  $\text{cm.}^3$  of flame gases,  $N^o$ , is related to the total number of atoms in all states per  $\text{cm.}^3$  of flame gases,  $N$ , by the famous Boltzmann equation, namely  $N^o = Ng_o/B(T)$  where  $g_o$  is the statistical weight of the lowest (ground) state and  $B(T)$  is the partition function of the atom, i.e.,  $B(T) = \sum_i g_i e^{-E_i/kT}$  where  $g_i$  is the statistical weight of the state  $i$ ,  $E_i$  is the energy of state  $i$  above the ground state, and the summation is over-all states of the atom. For the case of the minimum detectable concentration,  $N_m^o = N_m g_o/B(T)$ . As previously discussed in Section II,  $B(T)$  is approximately given by  $g_o$  except for a few atoms with low lying atomic states, e.g., Cr. In this paper  $B(T)$  for the examples given is accurately expressed by  $g_o$  and so  $N_m^o$  is essentially the same as  $N_m$ . The above theory is still correct for transitions occurring to levels higher than the ground state if  $g_o$  is replaced by the statistical weight of the state involved.

Substituting for  $k_m^o$  and  $\overline{\Delta i_T}$  in equation [30], and solving for  $N_m$  one obtains

$$N_m = \frac{53.5 \Delta V_D B(T)}{\rho L \lambda_0^2 g_u A_t \mathcal{S}} \left( \left\{ \frac{2BMe_c}{\gamma T_f W H (A/F^2) I^o} + \chi^2 + (\xi I_c s / I^o)^2 \right\} \Delta f \right)^{1/2}. \quad [42]$$

The above equation was derived assuming that the output photodetector signal due to thermal emission, fluorescent emission of the resonance line, and incident light scattering was either negligible or corrected for. In Appendix E equations for  $N_m$  are derived for the case in which compensation is not made for thermal emission for several detection systems. The influence of fluorescent emission and light scattering are also considered in Appendix E.

The optimum slit width,  $W_o$ , can be obtained by minimizing equation [42] with respect to  $W$ , i.e., equating  $dN_m/dW$  to zero and solving for  $W$ . If  $s$  is given by  $s = (R_d W)^2 + s_c^2$  from equations [2] and [37], and if  $s_c$  is assumed constant with change in slit width, then  $W_o$ , in cm., is given by

$$W_o = \left( \frac{B_{Mec} I^0}{\gamma T_f H (A/F^2) (\xi I_c R_d)^2} \right)^{1/3} . \quad [43]$$

The minimum detectable concentrations in atoms/cm.<sup>3</sup> of flame gases can be converted to solution concentrations in moles/liter by use of the equation derived in Section II (equation [21]).

### Discussion and Calculations

When one attempts to calculate minimum detectable concentrations through the use of equations [42], [43], and [21], the need for further measurements of basic experimental parameters of atomic absorption flame spectrometry becomes apparent. One of the most important contributions of these equations is that they point out those areas most in need of further work. It is difficult to compare calculated limits of detectability with measured limits of detectability unless accurate absolute values of

$I^0$ ,  $I_c$ ,  $\chi$ ,  $\xi$ ,  $\psi$ , and the photomultiplier tube characteristics are stated. Also, more information is needed on  $\delta$  values and on the degree of compound dissociation and atomic ionization so that  $\beta$  may be calculated with some accuracy. Although the calculation of limits of detectability is at present hampered by this lack of information, equation [42] is still valuable in that it allows one to calculate the effect of varying one or more of the experimental parameters on the sensitivity of analysis, e.g., the effect of slit width or temperature on  $N_m$ .

Table 4 shows the results of calculations of the minimum detectable concentrations for two favorable cases. When one chooses a good instrument such as the Beckman DU or the Jarrell-Ash 500 mm. grating monochromator, a 1P28 photomultiplier detector, and flame conditions such as stoichiometric oxyhydrogen or oxyacetylene, then, assuming a reasonable value for  $I^0$  and using the optimum slit width, all the terms under the square root in equation [42] except  $\chi^2$  are negligible. It is assumed that correction has been made for the output signal of the detector due to thermal and fluorescent emission and light scattering. Thus for these conditions, which are of experimental importance, the value of  $N_m$  depends directly on  $\chi$  the fluctuation of the source intensity, and so equation [42] can be reduced to

$$N_m = \frac{53.5 \Delta V_{dB}(T)}{\rho L \lambda_o^2 g_u A_t \delta} \chi(\Delta f)^{1/2}. \quad [44]$$

Equation [44] is in agreement with the expectation that over a fairly broad range of experimental conditions, the sensitivity of atomic absorption flame spectrometry would be independent of instrumental parameters. For the case represented by equation [44] the limit of

TABLE 4

REPRESENTATIVE RESULTS IN ATOMIC ABSORPTION FLAME SPECTROMETRY FOR  
LIMITS OF DETECTABILITY IN ATOMS PER CM.<sup>3</sup> OF FLAME GASES  
FOR Na and Cd IN TWO FLAMES<sup>a</sup>

| Atomic Line             | Flame Temp.<br>°K.   |                      |
|-------------------------|----------------------|----------------------|
|                         | 2700 <sup>b</sup>    | 2850 <sup>c</sup>    |
| Na 5890 A. <sup>d</sup> | $1.1 \times 10^{10}$ | $5.6 \times 10^9$    |
| Cd 2288 A. <sup>e</sup> | $4.3 \times 10^{10}$ | $2.2 \times 10^{10}$ |

<sup>a</sup>  $\chi = 10^{-2}$ ,  $\Delta f = 1$ .

<sup>b</sup> Stoichiometric H<sub>2</sub>/O<sub>2</sub> flame with aqueous solution flow rate of about 2 cm.<sup>3</sup>/min., L = 0.5 cm.

<sup>c</sup> Stoichiometric C<sub>2</sub>H<sub>2</sub>/O<sub>2</sub> flame with aqueous solution flow rate of about 2 cm.<sup>3</sup>/min., L = 1 cm.

<sup>d</sup>  $\Delta v_D = 4.1 \times 10^9 \text{ sec.}^{-1}$  at 2700°K.,  $4.2 \times 10^9 \text{ sec.}^{-1}$  at 2850°K.;  
 $B(T) \approx g_o = 2, g_u = 4; \rho = 0.97; \lambda_o = 5.89 \times 10^{-5} \text{ cm.}; A_t = 1.3 \times 10^8 \text{ sec.}^{-1}; f = 0.43.$

<sup>e</sup>  $\Delta v_D = 4.6 \times 10^9 \text{ sec.}^{-1}$  at 2700°K.,  $4.7 \times 10^9 \text{ sec.}^{-1}$  at 2850°K.;  
 $B(T) \approx g_o = 1, g_u = 3; \rho = 1; \lambda_o = 2.29 \times 10^{-5} \text{ cm.}; A_t = 1.7 \times 10^8 \text{ sec.}^{-1}; f = 0.43$



detectability could be greatly improved only by an increase in path length (13) or an increase in the stability of the source. However, from equation [42] it may be seen that as the stability of the source is improved, other terms might become significant. The term  $(\xi I_{cs}/I_0)^2$  becomes important as the flame background increases, e.g., with the highly fuel rich flames frequently used with elements that form very stable oxides, or as the spectral slit width increases, e.g., with filter instruments. However, for the conditions listed under Table 4, the minimum detectable concentration may be calculated from equation [44].

The values of the parameters given in Table 4 were found as follows. The Doppler half width,  $\Delta\nu_D$ , can be obtained from the expression given by Mitchell and Zemansky (31)

$$\Delta\nu_D = \frac{2\sqrt{2R \ln 2}}{c} \nu_0 \left( \frac{T}{M_a} \right)^{1/2} = 7.15 \times 10^{-7} \nu_0 \left( \frac{T}{M_a} \right)^{1/2}, \quad [45]$$

where  $R$  is the gas constant in ergs/mole.  $^{\circ}\text{K.}$ ,  $c$  is the speed of light in cm./sec.,  $T$  is the absolute temperature, and  $M_a$  is the atomic weight in atomic mass units. Universal constants have been evaluated in the right hand part of equation [45]. Values of  $\delta$  in terms of the damping constant  $\underline{a} = (\Delta\nu_L/\Delta\nu_D) \sqrt{\ln 2}$  (where  $\Delta\nu_L$  is the Lorentz half width in  $\text{sec.}^{-1}$ ) have been tabulated by Poesner (33). The value of  $\underline{a}$  for Na 5890 A. was obtained from Hinnov and Kohn (22). Although the value of  $\underline{a}$  for Cd 2288 A. is not readily available, its value is estimated to be about the same as that given for Ag 3281 A. by Hinnov and Kohn (22). Other listings of  $\underline{a}$  values are to be found in James and Sugden (23),

Sobolev (37) and Mitchell and Zemansky (31). A fuller discussion of the shape of spectral lines and its effect on atomic absorption is contained in Appendix C. The calculation of  $\rho$  is discussed in Appendix D.

The results given in Table 4 in atoms/cm.<sup>3</sup> can be converted to solution concentration by the use of equation [21]. A minimum detectable concentration of  $5.6 \times 10^9$  atoms/cm.<sup>3</sup> of flame gases (for Na 5890 Å. at 2850°K. (43) and the conditions given in Table 4) corresponds to a solution concentration of about 0.5 p.p.m. The terms in equation [21] have been taken as follows:  $Q = 125$  cm.<sup>3</sup>/sec.,  $n_T/n_{298} = 1.2$ ,  $\phi = 2$  cm.<sup>3</sup>/min.,  $\epsilon = 0.5$ , and  $\beta = 0.04$ . If the flame cell length were increased to 10 cm. the limit of detectability would drop to 0.05 p.p.m. and if the cell length were 100 cm., the limit would be 0.005 p.p.m. (13). Flames in which compound formation and ionization are less, will result in a value of  $\beta$  greater than 0.04 and, therefore, a lower limit of detectability. The limit of detectability calculated for a 10 cm. long flame compares quite favorably with measured values in the literature (3,14) for slightly different flame conditions.

In Table 5 the shape of the  $N_m$  versus slit width,  $W$ , curve is illustrated for several sets of conditions. Because the shape of the  $N_m$  versus  $W$  curve is independent of the spectral line, it is not necessary to evaluate all factors in equation [42]. The terms outside the square root have been combined in a constant term  $K_s$ , and equation [42] has been rewritten in the form

$$N_m = K_s \left( \frac{2BMc\Delta f}{\gamma T_f W H (A/F^2) I^0} + \chi^2 \Delta f + (\xi I_c R_d / I^0)^2 W^2 \Delta f \right)^{1/2}, \quad [46]$$

where  $s$  has been replaced by  $R_d W$  from equation [2].

TABLE 5

VARIATION OF  $N_m$  WITH  $W$  FOR SEVERAL MONOCHROMATORS AND FOR SEVERAL FLAME TYPES<sup>a</sup>

| Monochromator | Jarrell-Ash <sup>b</sup>                    |                                                            | DU <sup>c</sup>                |                                               | DU <sup>d</sup>                             |                                                            |
|---------------|---------------------------------------------|------------------------------------------------------------|--------------------------------|-----------------------------------------------|---------------------------------------------|------------------------------------------------------------|
| Flame Type    |                                             |                                                            |                                |                                               |                                             |                                                            |
| W (cm.)       | H <sub>2</sub> /O <sub>2</sub> <sup>e</sup> | C <sub>2</sub> H <sub>2</sub> /O <sub>2</sub> <sup>f</sup> | H <sub>2</sub> /O <sub>2</sub> | C <sub>2</sub> H <sub>2</sub> /O <sub>2</sub> | H <sub>2</sub> /O <sub>2</sub> <sup>g</sup> | C <sub>2</sub> H <sub>2</sub> /O <sub>2</sub> <sup>h</sup> |
| 0.02          | 10 <sup>-2</sup>                            | 10 <sup>-2</sup>                                           | 10 <sup>-2</sup>               | 10 <sup>-2</sup>                              | 10 <sup>-2</sup>                            | 10 <sup>-2</sup>                                           |
| 0.2           | 10 <sup>-2</sup>                            | 10 <sup>-2</sup>                                           | 10 <sup>-2</sup>               | 10 <sup>-2</sup>                              | 10 <sup>-2</sup>                            | 10 <sup>-2</sup>                                           |
| 2.0           | 10 <sup>-2</sup>                            | 10 <sup>-2</sup>                                           | 10 <sup>-2</sup>               | 10 <sup>-2</sup>                              | 10 <sup>-2</sup>                            | 10 <sup>-2</sup>                                           |
| 20            | 10 <sup>-2</sup>                            | 10 <sup>-2</sup>                                           | 10 <sup>-2</sup>               | 1.1 x 10 <sup>-2</sup>                        | 10 <sup>-2</sup>                            | 10 <sup>-2</sup>                                           |
| 200           | 10 <sup>-2</sup>                            | 1.2 x 10 <sup>-2</sup>                                     | 10 <sup>-2</sup>               | 4.5 x 10 <sup>-2</sup>                        | 1.1 x 10 <sup>-2</sup>                      | 2.8 x 10 <sup>-2</sup>                                     |

<sup>a</sup>B = 1.5; M = 10<sup>6</sup>;  $e_c = 1.6 \times 10^{-19}$  coul.;  $I^0 = 8.9 \times 10^{-4}$  watts/cm.<sup>2</sup> ster.;  $\gamma = 5.3 \times 10^4$  amps./watt at 400 mμ,  $1.2 \times 10^4$  amps./watt at 600 mμ;  $T_f = 0.5$ ; H = 1 cm.; A = 25 cm.<sup>2</sup>; F = 50 cm.;  $\chi = 10^{-2}$ ;  $\xi = 0.005$ ; s =  $R_d W$ .

<sup>b</sup> $R_d = 16$  mμ/cm.

<sup>c</sup> $R_d = 100$  mμ/cm. at 400 mμ.

<sup>d</sup> $R_d = 350$  mμ/cm. at 600 mμ.

<sup>e</sup> $I_c = 1.3 \times 10^{-8}$  watts/cm.<sup>2</sup> ster. mμ at 400 mμ.

<sup>f</sup> $I_c = 4.0 \times 10^{-7}$  watts/cm.<sup>2</sup> ster. mμ at 400 mμ.

<sup>g</sup> $I_c = 1.0 \times 10^{-8}$  watts/cm.<sup>2</sup> ster. mμ at 600 mμ.

<sup>h</sup> $I_c = 6.8 \times 10^{-8}$  watts/cm.<sup>2</sup> ster. mμ at 600 mμ.

(All  $N_m$  values in the above table have been divided by the constant factor  $K_s$ .)

In these calculations typical values of  $B$ ,  $M$ , and  $\gamma$  are taken for a 1P28 photomultiplier, and  $I^0$  is estimated to be approximately the value given by Crosswhite (11) for a typical line of an iron HCDT. The values of  $\chi$  and  $\xi$  have been estimated as shown in the table, and  $I_c$  has been taken from the work by Gilbert (17). For the chosen conditions,  $W$  would have to be unreasonably small before the first term in equation [46] would become significant. For this reason  $N_m$  shows no increase as the slit width is decreased below the calculated optimum value ( $W_0 = 0.19$  cm.). However, slit widths below 0.19 cm. will result in a smaller photodetector signal and correspondingly greater chance for electronic noise interference. As the slit width is increased beyond the optimum value,  $N_m$  increases very slowly for the conditions chosen, due to the increase in the last term in equation [46], and very wide slits could be used before the increase would become significant. In this case the slit width used would be determined by the mechanical slit width available on the instrument or by the proximity of other spectral lines. In such instances interference filters can be used with excellent results.

The difference in results between the Jarrell-Ash and the Beckman DU is due only to the difference in reciprocal linear dispersion in the two instruments. The variation in results with flame type is due only to the variation in flame background intensity. The variation with wavelength is a result of two competing factors. The flame background intensity is lower at 600 m $\mu$  than at 400 m $\mu$  by about 6-fold for an oxyacetylene flame, but the reciprocal linear dispersion of the DU is about 3.5 times higher at 600 m $\mu$  than at 400 m $\mu$ . The result is a slower increase in  $N_m$  at 600 m $\mu$  than at 400 m $\mu$  for the oxyacetylene

flame. For the oxyhydrogen flame the results are reversed since the flame background intensity is about the same at both wavelengths, and the higher reciprocal linear dispersion leads to a faster increase of  $N_m$  with  $W$  at 600  $m\mu$  than at 400  $m\mu$ .

The effect on  $N_m$  of varying other factors than those discussed above can be determined by examination of equation [42].

In Appendices C, D, and E some of the details of the preceding derivations and assumptions are discussed to a greater extent.

#### IV. CALCULATION OF OPTIMUM CONDITIONS

##### Introduction

A large number of factors affect the signal and the noise in both atomic emission and atomic absorption flame spectrometry, as may be seen from the signal and noise expressions presented in Sections II and III. At concentrations other than the minimum detectable, the expressions of interest for atomic emission flame spectrometry are:

$$i = K \gamma_{T_f WH} (A/F^2) n I, \quad [47]$$

and

$$\overline{\Delta i_T} = [2BMe_c \Delta f (i_d + \gamma_{T_f WH} (A/F^2) I_{cs}) + (\gamma_{T_f WH} (A/F^2) \overline{\Delta I_{cs}})^2 \Delta f]^{1/2}. \quad [48]$$

The expressions of interest for atomic absorption flame spectrometry are:

$$i^0 - i_t = \gamma_{T_f WH} (A/F^2) I^0 (1 - e^{-\rho k^0 L}), \quad [49]$$

and

$$\overline{\Delta i_T} = \left[ \left\{ \gamma_{T_f WH} (A/F^2) \right\}^2 \Delta f \left\{ \frac{2BMe_c I^0}{\gamma_{T_f WH} A/F^2} + (\overline{\Delta I^0})^2 + (\overline{\Delta I_{cs}})^2 + (\overline{\Delta I_s})^2 \right\} \right]^{1/2}. \quad [50]$$

However, from a practical point of view only a few factors are important in the discussion of optimum experimental conditions. The



analyst usually begins with a specified monochromator-detector-readout combination, which places such factors as  $T_f$ ,  $A$ ,  $F$ , and  $\Delta f$  beyond his control. The variables which the analyst is most often interested in optimizing are monochromator slit width,  $W$ , flame type (e.g.,  $C_2H_2/O_2$  or  $H_2/air$ ), and flame conditions (gas flow rates and solution flow rate).

If it is assumed, as in the preceding sections, that the entrance and exit slit widths are equal, then the relationship of the slit width to the signal and noise is evident from the above equations. The other factors affect the signal and the noise in a number of ways which are not immediately apparent. It may be seen that the flame background intensity  $I_c$  (or  $\overline{\Delta I_c}$ ), which is dependent on flame type, affects the noise,  $\overline{\Delta i_T}$ , in both atomic emission and atomic absorption flame spectrometry. Qualitatively it may be noted that the signal in both atomic emission and atomic absorption flame spectrometry is a function of the atomic concentration of the species of interest,  $N$ , in atoms/cm.<sup>3</sup> of flame gases, and the atomic concentration is dependent on compound dissociation and ionization, which depends on flame composition and flame temperature. In this section expressions will be derived relating the signal and the noise to flame type and flame conditions.

#### Selection of Optimum Slit Width

An expression for the optimum slit width as a function of experimental parameters for atomic emission and atomic absorption flame spectrometry may be obtained by maximizing the respective signal-to-noise ratios, i.e., differentiating the signal-to-noise ratio with

respect to  $W$ , equating to zero, and solving for the optimum slit width,  $W_0$ . The signal-to-noise ratio for atomic emission flame spectrometry is obtained by dividing equation [47] ( $K = 1$ ) by equation [48].

$$i/\overline{\Delta i_T} = \frac{\gamma_{T_f} W H(A/F^2) n I}{[2BMe_c \Delta f (i_d + \gamma_{T_f} W H(A/F^2) I_c s) + (\gamma_{T_f} W H(A/F^2) \overline{\Delta I_c} s)^2 \Delta f]^{1/2}} \quad [51]$$

The optimum slit width for atomic emission flame spectrometry is most readily obtained by finding the minimum of the noise-to-signal ratio by differentiating the square of the inverse of the above equation, i.e.,

$$\begin{aligned} (\overline{\Delta i_T}/i)^2 &= (k_1 W)^{-2} [k_2 (i_d + k_3 W s) \\ &+ (k_4 W s)^2 \Delta f] \quad , \end{aligned} \quad [52]$$

where  $k_1 = \gamma_{T_f} H(A/F^2) n I$  ,

$k_2 = 2BMe_c \Delta f$  ,

$k_3 = \gamma_{T_f} H(A/F^2) I_c$  ,

$k_4 = \gamma_{T_f} H(A/F^2) \overline{\Delta I_c}$  .

If  $s$  is given with sufficient accuracy by  $R_d W$ , where  $R_d$  is the reciprocal linear dispersion of the monochromator in  $\text{m}\mu/\text{cm}$ ., then the optimum slit width is found to be given by

$$W_0 = \left[ \frac{2BMe_c i_d}{(\gamma_{T_f} H(A/F^2) \overline{\Delta I_c} (\Delta f)^{1/2} R_d)^2} \right]^{1/4} \quad [53]$$

This is the same expression as previously derived for the optimum slit width at the limit of detectability expression with respect to  $W$ . The case in which  $s$  is not given with sufficient accuracy by  $R_d W$  has also been discussed in Section II.

The signal-to-noise ratio for atomic absorption flame spectrometry is obtained by dividing equation [49] by equation [50].

$$(i^0 - i_t) / \overline{\Delta i_T} = \frac{\gamma T_f W H (A/F^2) I^0 (1 - e^{-\rho k^0 L})}{\left[ \left\{ \gamma T_f W H (A/F^2) \right\}^2 \Delta f \left\{ \frac{2 B Me_c I^0}{\gamma T_f W H A / F^2} + (\overline{\Delta I^0})^2 + (\overline{\Delta I_{cs}})^2 + (\overline{\Delta I_s})^2 \right\} \right]^{1/2}} \quad [54]$$

As in the above case for atomic emission, the optimum slit width expression is most readily obtained by minimizing the noise-to-signal ratio by differentiating the square of the inverse of equation [54], i.e.,

$$[\overline{\Delta i_T} / (i^0 - i_c)]^2 = \quad [55]$$

$$(k_5 W)^{-2} \left[ (k_6 W)^2 \Delta f \left\{ k_7 W^{-1} + (\overline{\Delta I^0})^2 + (\overline{\Delta I_{cs}})^2 + (\overline{\Delta I_s})^2 \right\} \right],$$

where  $k_5 = \gamma T_f H (A/F^2) I^0 (1 - e^{-\rho k^0 L})$ ,

$$k_6 = \gamma T_f H (A/F^2),$$

$$k_7 = 2 B Me_c I^0 / (\gamma T_f H A / F^2).$$

The exact expression for  $s$  may be substituted into equation [55] without overly complicating the results, i.e.,  $s = (R_d^2 W^2 + s_c^2)^{1/2}$ . The various expressions for spectral slit width have been more fully discussed in Section II. If the indicated operations are carried out after substituting for  $s$  in equation [55], the optimum slit width expression is found to be

$$W_o = \left[ \frac{B Me_c I^0}{(\overline{\Delta I_c} R_d)^2 \gamma T_f H A / F^2} \right]^{1/3} \quad [56]$$

As might be expected this is the same expression as previously obtained by minimizing the limit of detection expression for atomic absorption flame spectrometry with respect to slit width.

### Effect of Flame Conditions on Atomic Concentration

The selection of optimum flame conditions is a somewhat more difficult problem than the selection of an optimum slit width. The origin of this difficulty resides in the nature of the flame source. The temperature of the flame source and the composition of the flame gases affect the atomic concentration of the species of interest through compound formation and ionization, but the flame temperature and flame gas composition cannot be chosen independently. There exists for any given flame a relatively narrow range of conditions of gas flow rates and fuel-to-oxygen ratios over which it is a stable, analytically useful flame, and for any given flame there is a relatively narrow temperature range (43) over which it can be adjusted. Therefore, an optimum temperature cannot be chosen in the same way that an optimum slit width can, because a major change in flame temperature involves a change in flame type (e.g., from  $C_2H_2/O_2$  to  $H_2/O_2$ ), with corresponding changes in  $I_c$ ,  $\overline{\Delta I_c}$ , and compound formation of the species of interest with flame gas constituents.

To find the optimum flame conditions the procedure which will be followed is to choose a particular flame and calculate the variation of the atomic concentration of the species of interest,  $N$ , and the variation of the signal-to-noise ratio over the temperature range which that flame can exhibit. The calculation of  $N$  and the signal-to-noise ratio then will be repeated for other flames. For both atomic emission and atomic absorption flame spectrometry, plots of signal-to-noise ratio versus temperature for several flame types will allow the selection of the optimum flame type for the particular analysis of interest.

The atomic concentration in the flame of the species of interest is, of course, related to the concentration of the solution aspirated into the flame, as well as being related to compound formation and ionization. No derivation of  $N$  is meaningful unless  $N$  can also be related to the solution concentration  $C$ . An expression has been derived in Section II (equation [21]) relating  $N$  and  $C$ . In slightly altered form this equation reads

$$N/\beta = 3 \times 10^{21} \frac{\phi n_{298} \epsilon C}{n_T Q T} . \quad [57]$$

In the following derivation it will be more convenient to relate  $C$  to  $P_T$ , the total pressure in atmospheres of the species of interest present in all forms, atomic, molecular, and ionic. The term  $N/\beta$  is the total concentration,  $N_T$ , in particles/cm.<sup>3</sup>, of the species of interest in all forms. Because  $N_T$  is small compared to other species for most flame spectrometric studies,  $N_T$  may be related to  $P_T$  by means of the ideal gas expression (30),  $P_T = N_T k T$ , where  $P_T$  is in atmospheres,  $k$  is the Boltzmann constant in cm.<sup>3</sup>-atm./°K. ( $1.38 \times 10^{-22}$ ), and  $T$  is the flame temperature in °K. The desired expression is, therefore,

$$P_T = 3 \times 10^{21} k \frac{\phi n_{298}}{Q n_T} \epsilon C . \quad [58]$$

For a given value of  $P_T$ , the equilibrium concentration of atoms of the species of interest present in the flame is dependent upon the dissociation of the aspirated salt, the formation of compounds with the flame gases, and ionization. If equilibrium is assumed,  $N$  can be predicted by consideration of the above processes. For the case in which an aqueous solution of sodium chloride is aspirated into the flame, the

formation of only one flame gas compound, NaOH need be considered (24).

Sodium chloride has been chosen as the aspirated salt because this is probably the most common means of introducing sodium into a flame, although no change in the results of the theory occur if  $\text{NaNO}_3$ ,  $\text{NaClO}_4$ , or other similar salts are considered. Most sodium salts, except NaOH, are completely dissociated at the temperature of flames used in flame spectrometry. The following equilibria expressions and their corresponding material balance expressions may be written for sodium aspirated as sodium chloride.

The dissociation of the aspirated salt,



has an equilibrium constant  $K_1$  given by

$$K_1 = \frac{p_{\text{Na}} p_{\text{Cl}}}{p_{\text{NaCl}}} , \quad [59]$$

where  $p_{\text{Na}}$ ,  $p_{\text{Cl}}$ , and  $p_{\text{NaCl}}$  are the partial pressures in atmospheres of Na, Cl, and NaCl, respectively. Assuming that Cl in the flame comes only from the dissociation of the salt, and that the pressure of HCl formed in the flame gases is a small fraction of the total pressure of Cl in the flame, and further assuming that  $p_{\text{NaCl}} \ll P_T$ , then  $p_{\text{Cl}}$  is given by

$$p_{\text{Cl}} = P_T - p_{\text{NaCl}} \cong P_T . \quad [60]$$

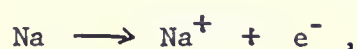
When using  $\text{H}_2/\text{O}_2$ ,  $\text{H}_2/\text{air}$ , and  $\text{C}_2\text{H}_2/\text{O}_2$  flames, the above assumptions



are valid. The stability of HCl is low (25), and so dissociation (see Appendix F) should be nearly complete. The stability of NaCl, as will be evident, is also low, and so the assumption  $P_T \gg P_{NaCl}$  is also valid. Substituting for  $p_{Cl}$  in equation [59] and solving for  $P_{NaCl}$  gives

$$P_{NaCl} = \frac{P_{Na} P_T}{K_1} . \quad [61]$$

For the ionization reaction



the equilibrium constant,  $K_2$ , is given by

$$K_2 = \frac{P_{Na^+} P_e}{P_{Na}} , \quad [62]$$

where  $P_{Na^+}$  is the partial pressure in atmospheres of sodium ions in the flame, and  $P_e$  is the partial pressure of electrons in the flame. The partial pressure of electrons in the flame is the sum of the partial pressures of electrons due to ionization of the flame gases and electrons due to ionization of the metal, i.e.,

$$P_e = p_e + P_{Na^+} , \quad [63]$$

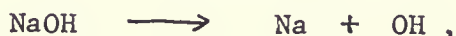
where  $p_e$  is the partial pressure in atmospheres of the flame gas electrons. Substituting for  $P_e$  in equation [62] gives

$$K_2 = \frac{P_{Na^+} P_e + P_{Na^+}^2}{P_{Na}} . \quad [64]$$

Solving for  $p_{\text{Na}^+}$  by the quadratic expression gives

$$p_{\text{Na}^+} = \frac{-p_e + (p_e^2 + 4K_2 p_{\text{Na}})^{1/2}}{2} . \quad [65]$$

For the dissociation reaction of the flame gas compound NaOH,



the equilibrium constant  $K_3$  is given by

$$K_3 = \frac{p_{\text{Na}} p_{\text{OH}}}{p_{\text{NaOH}}} , \quad [66]$$

where  $p_{\text{OH}}$  and  $p_{\text{NaOH}}$  are the partial pressures in atmospheres of OH and NaOH, respectively, present in the flame. Solving for  $p_{\text{NaOH}}$  gives

$$p_{\text{NaOH}} = \frac{p_{\text{Na}} p_{\text{OH}}}{K_3} . \quad [67]$$

Because  $P_T$  is the total pressure of the species of interest present in all forms,  $P_T$  is given by

$$P_T = p_{\text{Na}} + p_{\text{Na}^+} + p_{\text{NaCl}} + p_{\text{NaOH}} . \quad [68]$$

It may appear that the forms NaH and NaO should also be present in equation [68], but it was theoretically verified from dissociation constants of NaH and NaO that even in flames of relatively large  $p_H$  and  $p_O$ , the NaH and NaO species are essentially completely dissociated. The influence of H atoms from the flame gases on the formation of HCl in the flame has not been considered because, as will be seen, the

dissociation of NaCl is essentially complete, and this effect will not produce any changes in the results of the theory. In Appendix F the effect of introduction of an excess of Cl into the flame is considered i.e., introduction of NaCl into the flame in the presence of HCl. Substituting for  $p_{\text{NaCl}}$ ,  $p_{\text{Na}^+}$ , and  $p_{\text{NaOH}}$  from equations [61], [65], and [67], one obtains

$$p_T = p_{\text{Na}} + \frac{-p_e + (p_e^2 + 4K_2 p_{\text{Na}})^{1/2}}{2} + \frac{p_{\text{Na}} p_T}{K_1} + \frac{p_{\text{Na}} p_{\text{OH}}}{K_3} . \quad [69]$$

Clearing fractions and combining terms, one obtains

$$2(K_1 K_3 + K_3 p_T + K_1 p_{\text{OH}}) p_{\text{Na}} + K_1 K_3 (p_e^2 + 4K_2 p_{\text{Na}})^{1/2} - K_1 K_3 (2p_T + p_e) = 0 . \quad [70]$$

In order to use equation [70], the equilibrium constants  $K_1$ ,  $K_2$ , and  $K_3$  must be known at several temperatures over the temperature range of the flames of interest. The partial pressure of OH,  $p_{\text{OH}}$ , and the partial pressure of flame gas electrons,  $p_e$ , must also be known for the flames of interest. These factors,  $p_{\text{OH}}$  and  $p_e$ , are characteristic of the particular flames and vary somewhat with temperature. However, in the calculations to follow,  $p_{\text{OH}}$  and  $p_e$  will be assumed to be constant over the temperature range of a particular flame.

Solution of equation [70] for  $p_{\text{Na}}$  for a particular flame and a number of values of  $p_T$  is somewhat tedious (a graphical method seems to be the easiest), but fortunately two limiting cases which are of practical importance may be noted in which equation [70] can be greatly simplified. In most of the calculations reported in this paper, one or the other of the simplified forms can be used.

In the first case, if ionization of the sodium atoms is unimportant, i.e.,  $p_e^2 \gg 4K_2P_{Na}$ , then equation [70] becomes

$$(K_1K_3 + K_3P_T + K_1POH)P_{Na} - K_1K_3P_T = 0, \quad [71]$$

and equation [71] is readily solved for  $P_{Na}$

$$P_{Na} = \frac{K_1K_3P_T}{K_1K_3 + K_3P_T + K_1POH}. \quad [72]$$

The second case occurs when the partial pressure of flame gas electrons becomes negligible when compared to those produced by ionization of the metal. In this case  $(4K_2P_{Na})^{1/2} \gg p_e$  and equation [70] becomes

$$(K_1K_3 + 2K_3P_T + 2K_1POH)P_{Na} + K_1K_3K_2^{1/2}P_{Na}^{1/2} - 2K_1K_3P_T = 0. \quad [73]$$

Equation [73] is in the form of a quadratic equation in which  $P_{Na}^{1/2}$  is the variable. Solving by the quadratic expression and squaring gives

$$P_{Na} = \left[ \frac{-K_1K_3K_2^{1/2} + \{(K_1K_3K_2^{1/2})^2 + 4(K_1K_3 + K_3P_T + K_1POH)K_1K_3P_T\}^{1/2}}{2(K_1K_3 + K_3P_T + K_1POH)} \right]^2. \quad [74]$$

The partial pressure in atmospheres of Na,  $P_{Na}$ , can be converted by the ideal gas expression (30) to  $N$ , the atomic concentration of Na in the flame in atoms/cm.<sup>3</sup>, i.e.,

$$N = P_{Na}/kT, \quad [75]$$

where  $k$  is the Boltzmann constant in  $\text{cm}^3\text{-atm./}^\circ\text{K}$ . Therefore, multiplying either equation [70], equation [72], or equation [74] by  $1/kT$  allows the calculation of  $N$  as a function of temperature for a number of flame types and a number of values of  $P_T$  (and because  $P_T$  is related to the solution concentration by equation [51],  $N$  can be calculated at any value of solution concentration).

The results of the calculation of  $N$  are shown in Figure 1, where  $\log N$  is plotted versus  $T$  for seven values of  $P_T$  and three different flame types. From Figure 1, the effects of compound dissociation and ionization may be seen, as well as how these competing factors change with  $P_T$  and with flame type. As  $P_T$  increases the maxima of the curves, i.e., the temperatures at which ionization becomes more important than further compound dissociation, shift to higher temperatures. As  $P_{OH}$  decreases, e.g., in going from the  $\text{C}_2\text{H}_2/\text{O}_2$  flame to the  $\text{H}_2/\text{O}_2$  flame, the maxima of the curves are seen to appear at lower temperatures.

In all the calculations whose results are shown in Figure 1, the compound  $\text{NaCl}$  was found to be completely negligible with respect to  $\text{NaOH}$ . The results shown in Figure 1 would be exactly the same if other salts, such as  $\text{NaNO}_3$ , and  $\text{NaClO}_4$ , with dissociation constants similar to  $\text{NaCl}$ , were used for the aspirated species.

#### Optimum Flame Conditions for Atomic Emission Flame Spectrometry

Figure 1 is very useful for the discussion of the effects of compound formation and ionization, but the signal-to-noise ratio is needed for the selection of optimum conditions. The signal for atomic emission flame spectrometry is given by equation [47]. In seeking the optimum

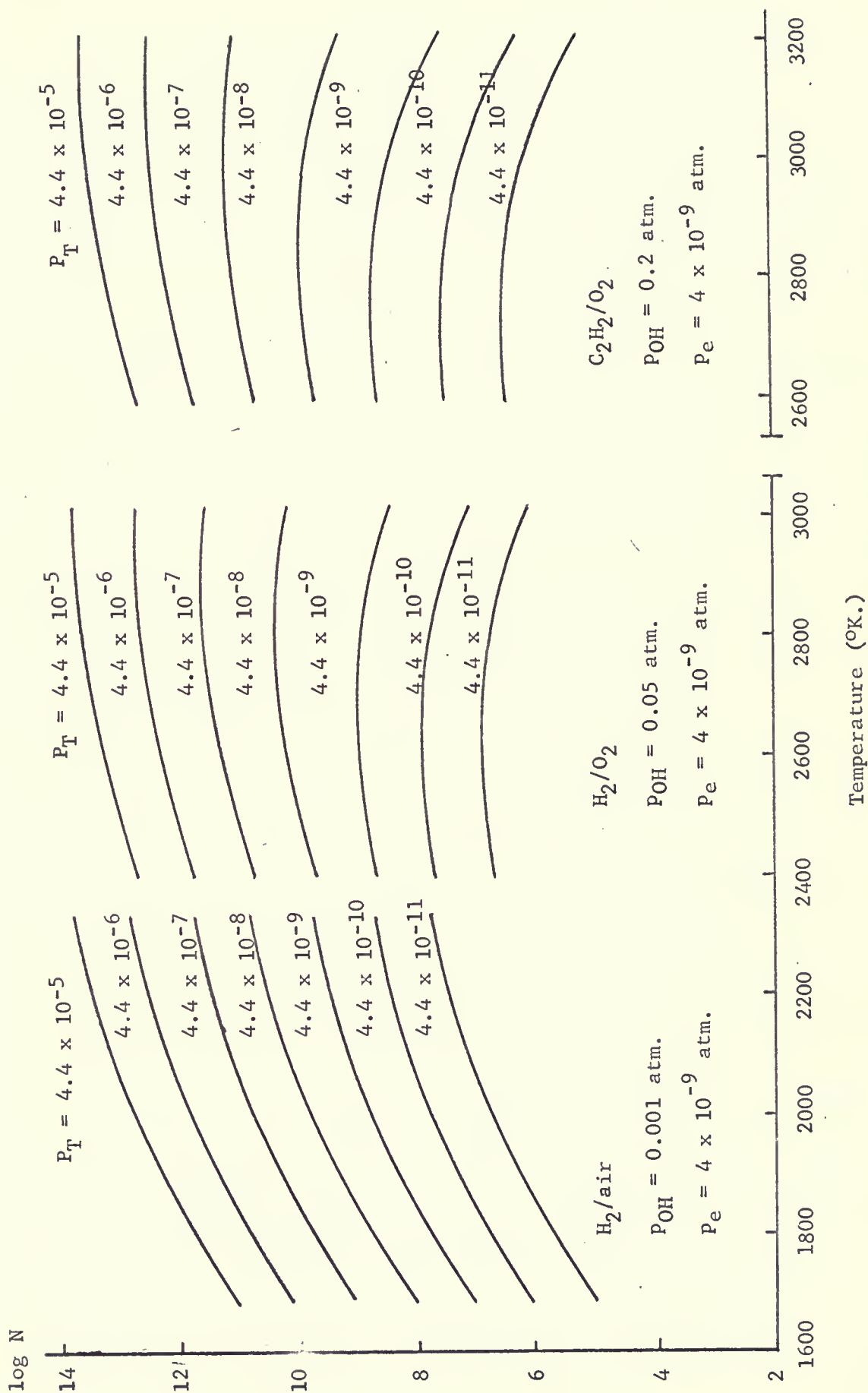


Figure 1. Calculated Plots of Atomic Concentration of Sodium Versus Flame Temperature for Several Total Pressures of Sodium and for Several Flame Types.



flame conditions the instrumental parameters, except  $W$ , will remain constant because the object sought is the flame type which will give the largest signal-to-noise ratio for a given instrument. Therefore equation [47] may be rewritten, using the optimum slit width expression, equation [53], to give

$$i = k_8 (\overline{\Delta I_c})^{-1/2} I, \quad [76]$$

$$\text{where } k_8 = \gamma T_f H(A/F^2)_n \left[ \frac{2BMe_c i_d}{(\gamma T_f H(A/F^2) (\Delta f)^{1/2} R_d)^2} \right]^{1/4}.$$

In the evaluation of  $k_8$  it is assumed that  $K$  is unity.

The relative signal for each flame type can then be calculated by substitution of the proper value of  $\overline{\Delta I_c}$  and the proper integrated intensity expression into equation [76]. However, the evaluation of  $I$ , the integrated intensity, is complicated by the fact that a plot of  $I$  versus sodium concentration would show two distinct regions of the curve. (See Appendix G for a further discussion of the intensity of spectral lines.) In the low concentration region the integrated intensity is proportional to the first power of  $N$  and is in fact given by

$$I = \frac{h\nu_o g_u}{10^7 4\pi B(T)} N A_t L e^{-E_u/kT}, \quad [77]$$

where all the terms have been previously defined. In the high concentration (or self-absorption) region, the integrated intensity in watts/cm.<sup>2</sup> ster. is proportional to the square root of  $N$  and is given by

$$I = \frac{h\nu_o^2}{10^7 c} e^{-E_u/kT} \left( \frac{\Delta\nu_D g_u}{\pi \sqrt{\ln 2} B(T)} a N A_t L \right)^{1/2}, \quad [78]$$

There is, of course, a small intermediate region in which the integrated intensity expression corresponds to neither of the above expressions. However,  $N$  can be converted to integrated intensity values with sufficient accuracy by extrapolating from the extremes to find the point of intersection of the two regions (i.e., some value of  $N$  which would give the same value of  $I$  by either expression), and using equation [77] for  $N$  values below this point and equation [78] for  $N$  values above this point. If equations [77] and [78] are equated at  $N$  equals  $N_i$ , then the intersection point,  $N_i$ , is found to be given by

$$N_i = \frac{16\pi a \Delta V_D B(T)}{\sqrt{\ln 2} A_t L \lambda_o^2 g_u} . \quad [79]$$

Therefore, for  $N$  values less than  $N_i$  the detector output signal for atomic emission flame spectrometry,  $i$ , can be calculated by the expression

$$i = k_8 k_9 (\overline{\Delta I_c})^{-1/2} L N e^{-E_u/kT} , \quad [80]$$

i.e., equation [77] is introduced into equation [76], and

$$k_9 = \frac{h \nu_o g_u}{1074 \pi B(T)} A_t .$$

For  $N$  values greater than  $N_i$  the detector output signal can be calculated by the expression

$$i = k_8 k_{10} (\overline{\Delta I_c})^{-1/2} L^{1/2} N^{1/2} e^{-E_u/kT} , \quad [81]$$

i.e., equation [78] is introduced into equation [76], and

$$k_{10} = \frac{h \nu_o^2}{107c} \left( \frac{\Delta V_D g_u}{\pi \sqrt{\ln 2} B(T)} a A_t \right)^{1/2} .$$

For convenience in further calculations, the constant  $k_{10}$  can be written in terms of the constant  $k_9$ . Of course, continuity exists at  $N = N_i$ , and so equation [80] and equation [81] will give the same value of  $i$  at the atomic concentration  $N_i$ , i.e.,

$$k_8 k_9 (\overline{\Delta I_c})^{-1/2} L N_i e^{-E_u/kT} = k_8 k_{10} (\overline{\Delta I_c})^{-1/2} L^{1/2} N_i^{1/2} e^{-E_u/kT}, \quad [82]$$

and solving for  $k_{10}$  gives

$$k_{10} = k_9 L^{1/2} N_i^{1/2}. \quad [83]$$

Substituting from equation [83] for  $k_{10}$ , equation [81] can be rewritten to give

$$i = k_8 k_9 (\overline{\Delta I_c})^{-1/2} L N_i^{1/2} e^{-E_u/kT}. \quad [84]$$

Equations [80] and [84] are altered slightly if more than one spectral line of the species of interest lies within the spectral slit width of the monochromator and, therefore, reaches the detector. This situation arises in the case of the sodium resonance doublet (5890, 5896 Å.), which is not resolved by the Beckman DU monochromator. The intensity of each of the lines making up the doublet is still given by equation [77] for the low concentration case and by equation [78] for the high concentration case.

If  $I_1$  is the intensity of line 1 (5890 Å.), and  $g_1$  is the statistical weight of the upper state of line 1, then for low concentrations

$$I_1 = \frac{h \nu_0 g_1}{10^7 4\pi B(T)} N A_t L e^{-E_u/kT}. \quad [85]$$

If  $I_2$  is the intensity of line 2 (5896 Å.), and  $g_2$  is the statistical weight of the upper state of line 2, then for low concentrations

$$I_2 = \frac{h\nu_o g_2}{10^7 4\pi B(T)} N A_t L e^{-E_u/kT} . \quad [86]$$

Because  $\nu_o$ ,  $A_t$ , and  $E_u$  are essentially the same for both lines, the same values can be used in both equations [85] and [86] without introducing significant error. For the high concentration case the intensities of lines 1 and 2 are given by

$$I_1 = \frac{h\nu_o^2}{10^7 c} e^{-E_u/kT} \left( \frac{\Delta\nu_{Dg1}}{\pi \sqrt{\ln 2} B(T)} a N A_t L \right)^{1/2} , \quad [87]$$

$$I_2 = \frac{h\nu_o^2}{10^7 c} e^{-E_u/kT} \left( \frac{\Delta\nu_{Dg2}}{\pi \sqrt{\ln 2} B(T)} a N A_t L \right)^{1/2} . \quad [88]$$

Equation [76] for the detector output signal for the case of an unresolved doublet is then given by

$$i = k_8 (\overline{\Delta I_c})^{-1/2} (K_1 I_1 + K_2 I_2) , \quad [89]$$

where  $K_1$  is the slit function factor for line 1 and  $K_2$  is the slit function factor for line 2. The evaluation of  $K$  for each spectral component can be carried out by use of equation [6] in Section II, i.e.,

$$K = 1 - \frac{|\lambda - \lambda_o|}{s} . \quad [6]$$

For the Na 5890, 5896 Å. doublet, when using the Beckman DU monochromator ( $R_d = 330$  mp/cm. at 5890 Å.), if the wavelength setting of the monochromator is 5892 Å. (nearer the stronger line), and if the

monochromator slit width is 0.01 cm., then  $s = R_d W = 3.3 \text{ mm}$ ,  $K_1 = 0.94$ , and  $K_2 = 0.88$ .

Substituting the proper intensity expressions into equation [89] and collecting terms shows that for low concentrations the detector output signal for atomic emission flame spectrometry is given by

$$i = k_8 (\overline{\Delta I_c})^{-1/2} \frac{h\nu_o A_t}{10^7 4\pi B(T)} N L e^{-E_u/kT} (K_1 g_1 + K_2 g_2) . \quad [90]$$

Collecting constant terms gives

$$i = k_8 k_{11} (\overline{\Delta I_c})^{-1/2} N L e^{-E_u/kT} , \quad [91]$$

where

$$k_{11} = \frac{h\nu_o A_t}{10^7 4\pi B(T)} (K_1 g_1 + K_2 g_2) .$$

At high concentrations the detector output signal is given by

$$i = k_8 (\overline{\Delta I_c})^{-1/2} \frac{h\nu_o^2}{10^7 c} e^{-E_u/kT} \left( \frac{\Delta\nu_D a N A_t L}{\pi \sqrt{\ln 2} B(T)} \right)^{1/2} [K_1 (g_1)^{1/2} + K_2 (g_2)^{1/2}] . \quad [92]$$

Collecting constant terms gives

$$i = k_8 k_{12} (\overline{\Delta I_c})^{-1/2} N^{1/2} L^{1/2} e^{-E_u/kT} , \quad [93]$$

where

$$k_{12} = \frac{h\nu_o^2}{10^7 c} \left( \frac{\Delta\nu_D a A_t}{\pi \sqrt{\ln 2} B(T)} \right)^{1/2} [K_1 (g_1)^{1/2} + K_2 (g_2)^{1/2}] .$$

By equating equation [91] to equation [93] when  $N$  equals  $N_i$ , it is possible to evaluate  $k_{12}$  in terms of  $k_{11}$ , i.e.,

$$k_{12} = k_{11} N_i^{1/2} L^{1/2} , \quad [94]$$

and  $i$  is then given by

$$i = k_8 k_{11} (\overline{\Delta I_c})^{-1/2} N_i^{1/2} N^{1/2} L e^{-E_u/kT} . \quad [95]$$

Equation [79] for the value of  $N$  at the intersection point,  $N_i$ , is also altered for the case in which the doublet is not resolved. In this case  $N_i$  is given by

$$N_i = \frac{16\pi B(T) \Delta V_D a [K_1(g_1)^{1/2} + K_2(g_2)^{1/2}]^2}{A_c L \lambda_o^2 \sqrt{\ln 2} (K_1 g_1 + K_2 g_2)^2} . \quad [96]$$

It should be noted at this point that the optimum slit width for atomic emission flame spectrometry was derived with the assumption that the spectral line of interest was single, sharp, and isolated. This assumption is not valid for the analysis of Na using the Beckman DU monochromator. The value of  $I$  in equation [51] should be replaced by  $I = K_1 I_1 + K_2 I_2$ . Because  $K_1$  and  $K_2$  are dependent on the slit width,  $W$ ,  $I$  is in this case dependent on the slit width. Fortunately the dependence of  $I$  on  $W$  is slight because  $K_1$  and  $K_2$  are close to unity (see example of calculation of  $K_1$  and  $K_2$  above), and the dependence of  $I$  on  $W$  will always be slight when the spectral lines are close together, and the spectral slit width,  $s$ , is large.

Calculation of the total root-mean-square photodetector output noise,  $\overline{\Delta i_T}$ , for atomic emission flame spectrometry can readily be accomplished by assuming that  $I_c$  (and the fluctuation in  $I_c$ ,  $\overline{\Delta I_c}$ ) is



approximately constant over the temperature range of any given flame. This assumption should not affect the results of the prediction of the optimum flame type, because the variation of  $I_c$  over the temperature range of a given flame is quite small, whereas the variation of  $I_c$  in going from one type flame to another is quite great (17).

When the proper optimum slit width is used in equation [48] for calculating  $\overline{\Delta i_T}$ , the value of  $\overline{\Delta i_T}$  will be approximately the same for each flame type. Qualitatively this could have been anticipated because optimization of the slit width results in obtaining the slit width at which the noise due to flame flicker ( $\gamma T_f W H (A/F^2) \overline{\Delta I_c} (\Delta f)^{1/2} s$ ) is reduced to approximately the same value as the noise due to the dark current shot effect ( $[2 B M e_c i_d]^{1/2}$ ). A decrease in the slit width below the optimum value does not result in an appreciable decrease in the noise, because the dark current noise does not depend on  $W$ . Because for a given detector the dark current is the same no matter which flame is used,  $\overline{\Delta i_T}$  is approximately the same for all flame types if the optimum slit width is used. Table 6 shows values of  $W_0$  and  $\overline{\Delta i_T}$  for three flames, calculated using the values listed under the table, which are typical values for a Beckman DU monochromator at 5890 A., a 1P28 photomultiplier, and a total consumption atomizer-burner.

Because  $\overline{\Delta i_T}$  is approximately the same for all three flame types, the flame type giving the maximum signal will also give the maximum signal-to-noise ratio. For low concentrations where the signal,  $i$ , is given by equation [80], the signal-to-noise ratio is given by

$$i/\overline{\Delta i_T} = k_c (\overline{\Delta I_c})^{-1/2} L N e^{-E_u/kT} , \quad [97]$$

TABLE 6  
OPTIMUM SLIT WIDTH AND TOTAL ROOT-MEAN-SQUARE NOISE  
FOR THREE FLAMES

| Flame                                         | $W_O$ (cm.)          | $\overline{\Delta i_T}$ (amps.) |
|-----------------------------------------------|----------------------|---------------------------------|
| H <sub>2</sub> /air                           | $6.1 \times 10^{-2}$ | $3.2 \times 10^{-10}$           |
| H <sub>2</sub> /O <sub>2</sub>                | $1.7 \times 10^{-2}$ | $3.1 \times 10^{-10}$           |
| C <sub>2</sub> H <sub>2</sub> /O <sub>2</sub> | $6.5 \times 10^{-3}$ | $3.2 \times 10^{-10}$           |

The following values were taken as typical for a Beckman DU monochromator and a 1P28 photomultiplier:  $B = 1.5$ ,  $M = 10^6$ ,  $e_c = 1.6 \times 10^{-19}$  coulombs,  $i_d = 10^{-7}$  amps.,  $\gamma = 10^4$  amps./watt,  $T_f = 0.5$ ,  $H = 1$  cm.,  $A = 25$  cm.<sup>2</sup>,  $F^2 = 2500$  cm.<sup>2</sup>,  $R_d = 330$  mp/cm.,  $\Delta f = 1$ ,  $\overline{\Delta I_c} = 0.005 I_c$ ,  $I_c = 7.7 \times 10^{-10}$  watts/cm.<sup>2</sup> ster. mp for H<sub>2</sub>/air (17),  $I_c = 9.7 \times 10^{-9}$  watts/cm.<sup>2</sup> ster. mp for H<sub>2</sub>/O<sub>2</sub> (17), and  $I_c = 6.8 \times 10^{-8}$  watts/cm.<sup>2</sup> ster. mp for C<sub>2</sub>H<sub>2</sub>/O<sub>2</sub> (17).

where  $k_c = k_8 k_9 / \overline{\Delta i_T}$ . For high concentrations where the signal,  $i$ , is given by equation [84], the signal-to-noise ratio is given by

$$i/\overline{\Delta i_T} = k_c (\overline{\Delta I_C})^{-1/2} N_i^{1/2} N^{1/2} e^{-E_u/kT} . \quad [98]$$

For the case of the unresolved doublet spectral line (equations [91] and [95]), at low concentrations the signal-to-noise ratio is given by

$$i/\overline{\Delta i_T} = k_d (\overline{\Delta I_C})^{-1/2} N_L e^{-E_u/kT} , \quad [99]$$

where  $k_d = k_8 k_{11} / \overline{\Delta i_T}$ , and at high concentrations the signal-to-noise ratio is given by

$$i/\overline{\Delta i_T} = k_d (\overline{\Delta I_C})^{-1/2} N_i^{1/2} N^{1/2} L e^{-E_u/kT} . \quad [100]$$

Figure 2 shows plots of  $i/\overline{\Delta i_T} k_c$  versus  $T$ . The upper dashed line in Figure 2 is  $i/\overline{\Delta i_T} k_c$  at  $N = N_i$ , where  $N_i$  has been calculated from equation [79]. Below this dashed line  $k/\overline{\Delta i_T} k_c$  is calculated from equation [97]. Above this dashed line  $i/\overline{\Delta i_T} k_c$  is calculated from equation [98]. At low concentrations  $i/\overline{\Delta i_T} k_c = i/\overline{\Delta i_T} k_d = (\overline{\Delta I_C})^{-1/2} N_L e^{-E_u/kT}$ , i.e., the curves given in Figure 2 are valid whether a single spectral line or a multiplet passes through the spectral slit width. In this low concentration region the plotted signal-to-noise ratios are entirely independent of the instrument used, i.e., the optimum flame type can be determined without knowing what instrumental setup is to be used. The absolute value of the signal-to-noise ratio for a particular instrumental setup, flame type, and flame temperature can be calculated by evaluating  $k_c$  (or  $k_d$ ) by substituting values for the experimental parameters.

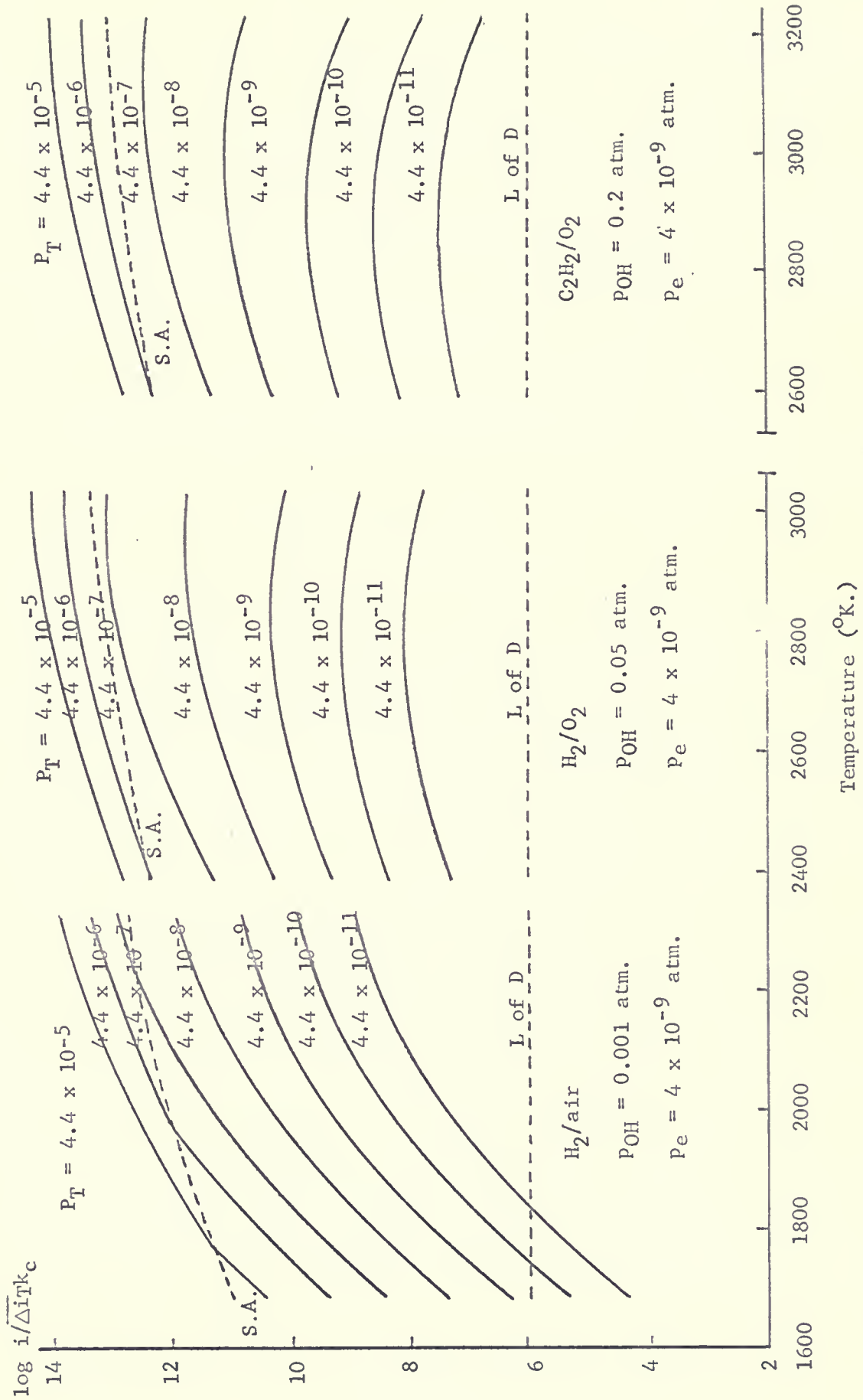


Figure 2. Calculated Plots of Signal-to-Noise Ratios for the Na 5890, 5896 A. Doublet Versus Flame Temperature for Several Total Pressures of Sodium and for Several Flame Types.

At high concentrations the plotted signal-to-noise ratio depends to a small extent on the instrumental setup because  $i/\overline{\Delta i_T} k_c$  depends on  $N_i$ , the value of which depends on whether the doublet is resolved or unresolved. When the spectral line is single (as the case would be when using the 0.5 meter Ebert mounting, Jarrell-Ash monochromator),  $N_i$  is calculated from equation [79]. When the spectral line is an unresolved doublet,  $N_i$  is calculated from equation [96]. The difference in values of  $N_i$  as calculated from equations [79] and [96] is small enough that neglecting the instrumental dependence of  $N_i$  will not affect the choice of the optimum flame type. This is especially true because the signal-to-noise ratios  $i/\overline{\Delta i_T} k_c$  or  $i/\overline{\Delta i_T} k_d$  depend only on the one-half power of  $N_i$ .

Neglecting the small instrumental dependence of the signal-to-noise ratios plotted in Figure 2, much information about optimum conditions for analysis of Na by atomic emission flame spectrometry may be obtained from Figure 2. The two dashed lines for each flame mark the upper and lower limits of an optimum region for that flame. The upper dashed line (S.A.), as previously discussed, indicates the beginning of the self-absorption region. Above this line the signal, and hence the signal-to-noise ratio, is proportional to the square-root of  $N$ , the atomic concentration. The lower dashed line (L. of D.) marks the limit of detectability for the Na 5890, 5896 Å. doublet for the particular flame when using a Beckman DU monochromator and a good 1P28 photomultiplier. The limit of detectability lines were obtained by calculating the limits of detectability in atoms/cm.<sup>3</sup> for Na in each of the three flames, at several temperatures, from equation [16]. From these

values of  $N$ ,  $i/\Delta i_T k_c$  values were calculated using equation [97]. The limit of detectability lines are the only lines on Figure 2 which depend to a great extent on the instrumental setup. The limit of detectability will be different with each monochromator-detector combination, and therefore this line must be calculated for specific cases.

In the region between the self-absorption line (S.A.) and the limit of detectability line (L. of D.), the spectral line is detectable and self-absorption of radiation is negligible. In the  $H_2/O_2$  flame at 2500°K. the point at which self-absorption becomes important corresponds to a  $P_T$  value of approximately  $4.4 \times 10^{-6}$  atmospheres. At an aqueous solution flow rate of approximately 2 cm.<sup>3</sup>/min. and gas flow rates of 2860 cm.<sup>3</sup>/min.  $O_2$  and 10,000 cm.<sup>3</sup>/min.  $H_2$ , this corresponds to a solution concentration of approximately  $2.3 \times 10^{-3} M$ , i.e., 53 p.p.m. ( $n_{298}/n_T = 1.2$ ,  $\epsilon = 0.5$ ). Also, in the  $H_2/O_2$  flame at a temperature of 2500°K., linear analytical curves for Na, free from the effects of self-absorption and ionization should be obtained for  $P_T$  values from approximately  $10^{-11}$  to  $10^{-6}$  atmospheres (or solution concentrations of approximately  $5.2 \times 10^{-9}$  to  $5.2 \times 10^{-4}$  moles/liter). A  $H_2/O_2$  flame at a temperature of 2500°K. should also give linear analytical curves for Na but with half the slope of the previous curves due to self-absorption for  $P_T$  values above approximately  $4 \times 10^{-6}$  atmospheres.

#### Optimum Flame Conditions for Atomic Absorption Flame Spectrometry

The optimum conditions for analysis by atomic absorption flame spectrometry can be determined in much the same way as for atomic emission flame spectrometry. The signal-to-noise ratio for atomic



absorption has been given in equation [54]. After dividing both numerator and denominator by  $\gamma_{T_fWH}(A/F^2)I^0$ , equation [54] can be rewritten as

$$(i^0 - i_t)/\overline{\Delta i_T} = \frac{1 - e^{-\rho k^0 L}}{\left[ \Delta f \left\{ \frac{2BMe_c}{\gamma_{T_fWH}(A/F^2)I^0} + (\overline{\Delta I^0}/I^0)^2 + (\overline{\Delta I_{cs}}/I^0)^2 + (\overline{\Delta I_s}/I^0)^2 \right\} \right]^{1/2}} . \quad [101]$$

When the optimum slit width,  $W_0$ , is used in equation [101],  $(\overline{\Delta I_{cs}}/I^0)^2$  is much smaller than  $(\overline{\Delta I^0}/I^0)^2$  and can be neglected. Substitution of values in the first term of the sum in the denominator of equation [101], shows that for any practical set of conditions this term will always be quite small when compared to  $(\overline{\Delta I^0}/I^0)^2$ , which will never have a value smaller than about  $10^{-4}$ . The last term,  $(\overline{\Delta I_s}/I^0)^2$ , will be small in most cases of practical importance in atomic absorption flame spectrometry. The intensity of the scattered radiation  $I_s$  is always a fraction of  $I^0$ . Usually the fraction is quite small, and the scattering term can be neglected. The fraction of scattered radiation could always be made small by using organic solvents or chamber-type atomizers to decrease the particle size of the aspirated solution in the flame. For the purposes of selecting the optimum flame conditions, equation [101] can be rewritten as

$$(i^0 - i_t)/\overline{\Delta i_T} = k_{13}(1 - e^{-\rho k^0 L}) , \quad [102]$$

where

$$k_{13} = [(\overline{\Delta I^0}/I^0)(\Delta f)^{1/2}]^{-1} .$$

The value of  $k^0$ , the atomic absorption coefficient at the line center (in  $\text{cm}^{-1}$ ), is given (31) by

$$k^0 = \frac{2 \sqrt{\ln 2} \lambda_0^2 g_u N A_t f}{\Delta \nu_D \sqrt{\pi} 8 \pi B(T)} . \quad [103]$$

An expression for the Doppler half-width,  $\Delta \nu_D$ , has already been given in Section III:

$$\Delta \nu_D = \frac{2 \sqrt{2R \ln 2}}{c} \nu_0 \left( \frac{T}{M_a} \right)^{1/2} . \quad [45]$$

After substituting  $\Delta \nu_D$  from equation [45] into equation [103], and the resulting expression for  $k^0$  into equation [102],  $(i^0 - i_t)/\overline{\Delta i_T}$  is found to be given by

$$(i^0 - i_t)/\overline{\Delta i_T} = k_{13} (1 - e^{-k_{14} NL/T^{1/2}}) , \quad [104]$$

where the terms which are not dependent on flame temperature or flame composition have been collected into the constant  $k_{14}$ , and

$$k_{14} = \frac{\rho 2 \sqrt{\ln 2} \lambda_0^2 g_u A_t f c M_a^{1/2}}{\sqrt{\pi} 8 \pi B(T) 2 \sqrt{2R \ln 2} \nu_0} .$$

If the spectral line of interest is not a singlet but a doublet, as in the case of the Na 5890, 5896 Å. doublet, which is not resolved by many monochromators, then equations [102], [103], and [104] must be altered. Equation [102] should read in this case

$$(i^0 - i_t)/\overline{\Delta i_T} = k_{13} (1 - e^{-\theta k^0 L}) , \quad [105]$$

where  $\theta$  is a factor to account for the line being multiple. The evaluation of  $\theta$  is discussed in Appendix H. The value of  $I^0$  in the

constant  $k_{13}$  is the sum of the intensities of the two lines making up the doublet, i.e.,  $I^0 = k_1 I^0_1 + k_2 I^0_2$ , where line 1 is the 5890 A. line, and line 2 is the 5896 A. line. The value of  $k^0$  is also altered. For a doublet  $k^0 = k^0_1 + k^0_2$ , where  $k^0_1$  and  $k^0_2$  are the atomic absorption coefficients at the line centers of line 1 and line 2, respectively. Therefore, equation [103] should read

$$k^0 = \frac{2 \sqrt{\ln 2} \lambda_0^2 N A_t \delta}{\Delta \nu_D \sqrt{\pi} 8 \pi B(T)} (g_1 + g_2) , \quad [106]$$

where  $g_1$  and  $g_2$  are the statistical weights of the upper states of lines 1 and 2, respectively, and  $\lambda_0$ ,  $A_t$ , and  $\Delta \nu_D$  are approximately the same for both lines. Equation [104] should read in this case

$$(i^0 - i_t)/\overline{\Delta i_T} = k_{13} (1 - e^{-k_{15} NL/T^{1/2}}) , \quad [107]$$

where

$$k_{15} = \frac{e 2 \sqrt{\ln 2} \lambda_0^2 (g_1 + g_2) A_t \delta \text{ cMa}^{1/2}}{\sqrt{\pi} 8 \pi B(T) 2 \sqrt{2R \ln 2} \nu_0} .$$

It may be seen from equations [104] and [107] that no matter which of the two expressions most accurately gives the value of the signal-to-noise ratio for atomic absorption flame spectrometry, when flame conditions are such that  $NL/T^{1/2}$  has its maximum value, the value of  $(i^0 - i_t)/\overline{\Delta i_T}$  will also be at its maximum. Figure 3 shows plots of  $\log (NL/T^{1/2})$  versus  $T$  for three flames and seven values of  $P_T$ . These plots have the advantage of being entirely independent of the instrument used, i.e., the same set of curves can be used to determine optimum flame conditions no matter what spectrometer is to be used in the

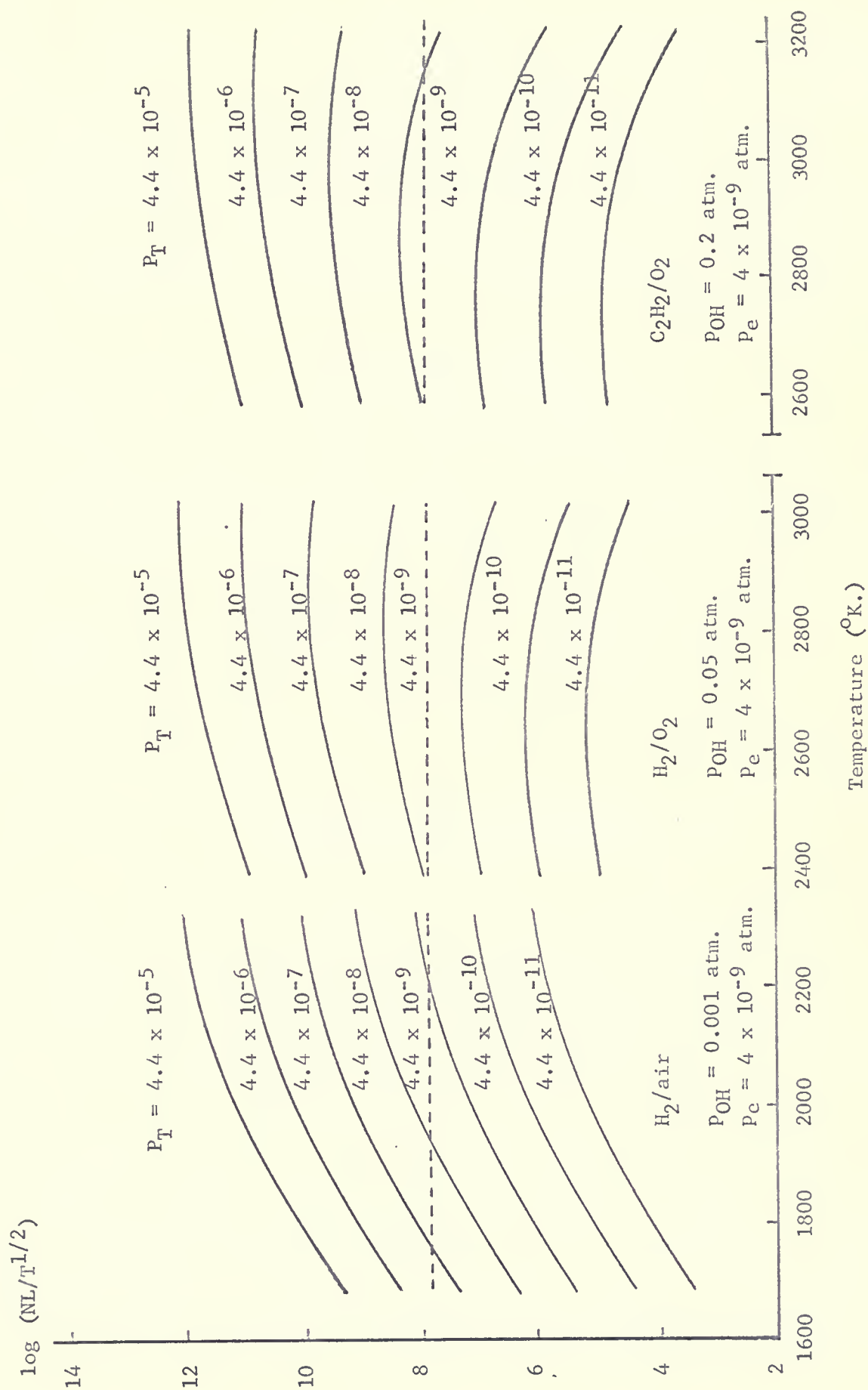


Figure 3. Calculated Plots of  $NL/T^{1/2}$  Versus Flame Temperature for Several Total Pressures of Sodium and for Several Flame Types.

analysis. The absolute value of the signal-to-noise ratio for atomic absorption can be obtained from Figure 3 by evaluating the constants in equations [104] or [107].

The dashed lines in Figure 3 mark the limits of detectability for the Na 5890, 5896 Å. doublet for the particular flame when using a Beckman DU monochromator and a 1P28 photomultiplier detector. The limits of detectability were calculated from equation [44]. The limits of detectability are, of course, dependent on the instrumental setup used and must be calculated for specific cases.

Although it is not indicated in Figure 3, there is an upper limit to the optimum region for analysis by atomic absorption flame spectrometry. Qualitatively it may be seen that an upper limit would be reached when the atomic concentration,  $N$ , reached a value such that the difference between the output signal due to the transmitted intensity when solvent is introduced into the flame,  $I^0$ , and the output signal due to the transmitted intensity when sample is introduced,  $I_t$ , becomes of the same order of magnitude as the noise. An equation for the maximum detectable concentration can be derived in much the same manner as for the minimum detectable concentration. However, the resulting equation is unduly complex and can only be solved graphically. It is not particularly important to be able to calculate the maximum detectable concentration because it is always possible to dilute concentrated solutions in order to work in a more favorable concentration region, and so the theory for the maximum detectable concentration is not presented in this paper.

### Calculations

The equilibrium constant for the dissociation of NaCl,  $K_1$ , as a function of temperature, is calculated from the expression given by Mavrodineanu and Boiteux (30),

$$\log K_1 = -5040 \frac{D_{\text{NaCl}}}{T} + \frac{3}{2} \log T + \log (1 - 10^{-0.625 \omega_e / T}) \\ + i_{\text{Na}} + i_{\text{Cl}} - i_{\text{NaCl}}, \quad [108]$$

where  $D_{\text{NaCl}}$  is the dissociation energy of NaCl in electron volts,  $\omega_e$  is the vibrational constant of the molecule in  $\text{cm}^{-1}$  (21), and  $i_{\text{Na}}$ ,  $i_{\text{Cl}}$ , and  $i_{\text{NaCl}}$  are the chemical constants of Na, Cl, and NaCl, respectively. For a monatomic gas (either Na or Cl) the chemical constant is given (30) by

$$i_M = -1.587 + \frac{3}{2} \log M_a + \log g_0, \quad [109]$$

where  $M_a$  is the atomic mass of the species of interest, and  $g_0$  is the statistical weight of the ground state of the atom. For a diatomic gas such as NaCl the chemical constant is given (30) by

$$i_{\text{NaCl}} = -1.738 + \frac{3}{2} \log M_{\text{NaCl}} + \log g_0^* - \log B_e, [110]$$

where  $M_{\text{NaCl}}$  is the molecular weight of NaCl,  $g_0^*$  is the statistical weight of the ground state of the molecule, and  $B_e$  is the rotational constant in  $\text{cm}^{-1}$  of the molecule (21).

The equilibrium constant for the ionization reaction,  $K_2$ , as a function of temperature is also calculated from an expression given by Mavrodineanu and Boiteux (30),



$$\log K_2 = -5040 V/T + 5/2 \log T + \log g_0' - \log g_0 - 6.1818, \quad [111]$$

where  $V$  is the ionization energy of the atom in electron volts,  $g_0$  is the statistical weight of the ground state of the neutral atom, and  $g_0'$  is the statistical weight of the ground state of the ion.

The equilibrium constant for the dissociation of NaOH,  $K_3$ , as a function of temperature is obtained from thermochemical data tabulated in the JANAF Tables (25). The values found for  $K_1$ ,  $K_2$ , and  $K_3$  are summarized in Table 7.

The partial pressure of flame electrons,  $p_e$ , is taken to be  $4 \times 10^{-9}$  atm. (15) in the outer cones of all three flames. The partial pressures of OH in the various flames are estimated from the information given by Zaer (46), and  $p_{OH}$  is assumed constant over the temperature range of the individual flames. In estimating the values of  $p_{OH}$ , it is necessary to take into account the solvent being aspirated into the flame because the solvent contributes a large portion of the flame gases. For the  $C_2H_2/O_2$  flame,  $p_{OH}$  is estimated to be 0.2 atm. In the  $H_2/O_2$  and  $H_2/air$  flames  $p_{OH}$  is estimated to be, respectively, 0.05 atm. and 0.001 atm.

The value of  $\overline{\Delta I_c}$  is estimated to be  $5 \times 10^{-3} I_c$ , where  $I_c$  has been measured for the various flames by Gilbert (17). Atomization efficiencies and flame temperatures are estimated from work performed in this laboratory (42,43). In calculating Figures 2 and 3,  $L$  is taken to be 1 cm. in all cases, because this is found to be approximately the radius of a flame in good adjustment. The value of  $E_u$  for Na is 2.1 electron volts (28).

TABLE 7  
VALUES OF  $K_1$ ,  $K_2$ , AND  $K_3$  AS A FUNCTION OF T

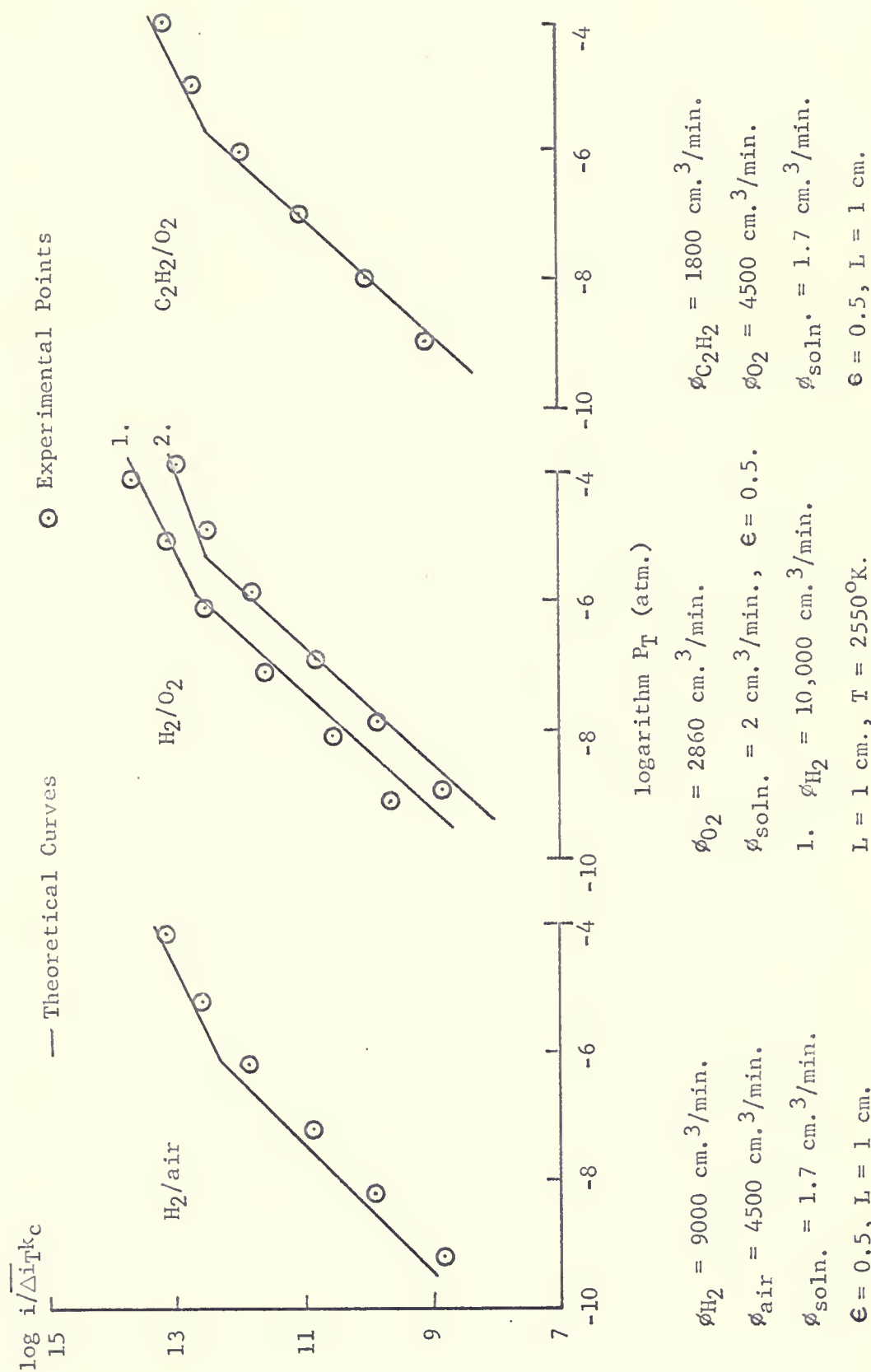
| T (°K.) | $K_1$ (atm.)         | $K_2$ (atm.)          | $K_3$ (atm.)         |
|---------|----------------------|-----------------------|----------------------|
| 1600    | $4.4 \times 10^{-7}$ | $2.5 \times 10^{-15}$ | $1.3 \times 10^{-7}$ |
| 2000    | $9.1 \times 10^{-5}$ | $6.4 \times 10^{-12}$ | $4.1 \times 10^{-5}$ |
| 2400    | $3.2 \times 10^{-3}$ | $1.5 \times 10^{-9}$  | $2.0 \times 10^{-3}$ |
| 2800    | $4.2 \times 10^{-2}$ | $7.4 \times 10^{-8}$  | $3.1 \times 10^{-2}$ |
| 3200    | $1.4 \times 10^{-1}$ | $1.6 \times 10^{-6}$  | $2.5 \times 10^{-1}$ |

In calculating  $N_1$  from equations [79] and [96], the value of  $a$  is taken from data given by Hinnov and Kohn (22). The Doppler half-width,  $\Delta_D$ , is calculated from equation [45], and  $B(T)$  is equal to  $g_0$ , the statistical weight of the ground state of Na. Spectral data, such as  $A_t$ ,  $g_u$ , and  $g_0$ , are taken from the Landolt-Börnstein tables (28).

### Experimental Verification of Theory

The validity of the theory developed in this paper has been shown by comparing theoretically predicted analytical (working) curves with experimentally determined analytical curves. The theoretical analytical curves were obtained from Figure 2 by choosing a temperature typical of the flame to be used (43) and then reading off  $P_T$  and corresponding  $\log (i/\Delta i_T k_c)$  values at that flame temperature. Because the signal-to-noise ratio is proportional to the signal, as previously discussed, plots of  $\log (i/\Delta i_T k_c)$  versus  $\log P_T$  will have the same shape and slope as the analytical curves of signal versus concentration.

The experimental curves were obtained by recording the output signal for a wide range of solution concentrations. Solution concentrations were converted to  $P_t$  values by equation [58] so that measured values of signal as a function of  $P_t$  were obtained. The measured curves of the logarithm of the signal versus  $\log P_T$  were shifted along the  $\log (i/\Delta i_T k_c)$  axis until the experimental curve for the  $C_2H_2/O_2$  flame coincided with the theoretical curve. The analytical curves for the  $H_2/O_2$  and  $H_2/air$  flames were shifted by the same factor as the  $C_2H_2/O_2$  flame curve. Agreement as to shape and slope of the two sets of curves for all three flames is quite good as shown in Figure 4.



|                                                       |                                                                      |                                                                |
|-------------------------------------------------------|----------------------------------------------------------------------|----------------------------------------------------------------|
| $\phi_{\text{H}_2} = 9000 \text{ cm.}^3/\text{min.}$  | $\phi_{\text{O}_2} = 2860 \text{ cm.}^3/\text{min.}$                 | $\phi_{\text{C}_2\text{H}_2} = 1800 \text{ cm.}^3/\text{min.}$ |
| $\phi_{\text{air}} = 4500 \text{ cm.}^3/\text{min.}$  | $\phi_{\text{soln.}} = 2 \text{ cm.}^3/\text{min.}, \epsilon = 0.5.$ | $\phi_{\text{O}_2} = 4500 \text{ cm.}^3/\text{min.}$           |
| $\phi_{\text{soln.}} = 1.7 \text{ cm.}^3/\text{min.}$ | 1. $\phi_{\text{H}_2} = 10,000 \text{ cm.}^3/\text{min.}$            | $\phi_{\text{soln.}} = 1.7 \text{ cm.}^3/\text{min.}$          |
| $\epsilon = 0.5, L = 1 \text{ cm.}$                   | $L = 1 \text{ cm.}, T = 2550^\circ\text{K.}$                         | $\epsilon = 0.5, L = 1 \text{ cm.}$                            |
| $T = 2100^\circ\text{K.}$                             | 2. $\phi_{\text{H}_2} = 5720 \text{ cm.}^3/\text{min.}$              | $T = 2700^\circ\text{K.}$                                      |
|                                                       | $L = 0.5 \text{ cm.}, T = 2500^\circ\text{K.}$                       |                                                                |

Figure 4. Calculated and Experimental Analytical Curves for the Na 5890, 5896 Å. Doublet for Several Flame Types.

It should be noted that Alkemade (1) predicted the shape of the sodium 5890, 5896 Å. flame emission analytical curve by deriving the "curves of growth" for the total absorption of the Na doublet. He had good correlation between the derived curves and the experimental curves. Alkemade (1), however, neglected the effects of ionization and compound formation on the shapes of the analytical curves and also did not calculate the intersection point of the curves. He used experimental conditions substantially different from those used in this paper; namely, a propane/air flame, a chamber type atomizer-burner, and a glass transmission filter for isolation of the sodium doublet. Even though experimental conditions were considerably different from those used in this paper, the basic theoretical results were quite similar.

The experimental analytical curves were determined on a Beckman DU with spectral energy recording attachment (SERA) and 1P28 photomultiplier detector. Efforts were made to have the measurement procedures agree as closely as possible with standard practices in order to illustrate the practical value of the theory developed in this paper. Analytical curves were determined for four flames with conditions as noted on the curves. The analytical curves shown in Figure 4 are average curves for quadruplicate measurements.

The Beckman flame housing attachment was used throughout, but the mirror in the housing was blocked so that only radiation coming directly from the flame entered the spectrometric system. Blocking of the mirror was necessary to insure reproducible entrance optics. Over the wide concentration range used in this study, the relative contributions of radiation arriving directly from the flame and radiation reflected by

the mirror changed as the concentration changed because of the variation of the amount of reflected radiation absorbed in passing through the flame gases. It was found that the ratio of meter reading with mirror unmasked to meter reading with mirror masked varied from 3.18 at  $10^{-1}$  p.p.m. Na to 2.06 at 1000 p.p.m. Na. If the mirror were not blocked, this would lead to curvature of the analytical curves not accounted for in the calculation of the theoretical curves. However, the influence of entrance optics could be accounted for by supplying the proper value of  $n$ , the entrance optics factor, to adjust the measured signal values (see equation [47]).

In determining the experimental curves the calculated optimum slit widths were used, and the sensitivity control was adjusted to keep the readings on scale. With the Beckman housing a large region was observed by the monochromator (approximately 1.6 cm. wide by 2.6 cm. high). With the setup used, the lower edge of this region was 1.1 cm. above the tip of the burner. The temperatures indicated for the different flames were estimated as average temperatures over the flame region viewed (43).

The solutions used in constructing the experimental curves had concentrations of  $10^{-2}$ ,  $10^{-1}$ , 1, 10, 100, and 1000 p.p.m. The solution of 1000 p.p.m. Na was prepared by dissolving the appropriate weight of NaCl in distilled water. The other solutions were prepared by successive dilutions. Lower solution concentrations were not used because of difficulties encountered with spurious Na emission, apparently attributable to dust particles in the air.

As may be seen in Figure 4, the position of the intersection points and the slopes of the experimental and theoretical curves agree quite



well. Because the  $H_2/O_2$  flame with the lower flow rate of  $H_2$  has a radius approximately half that of the other flames, the theoretical intersection point for this case was calculated using  $L = 0.5$  cm. This flame does not represent a practical case because the size of the flame is too small to be experimentally useful. However, it is interesting to note that the theory quite adequately accounts for the effect of flame size on the point at which self-absorption becomes important.

Note that in Figure 2, only one value of  $p_{OH}$  is given for  $H_2/O_2$  flames. Measurement of the OH emission in the outer cone of the flame at 3090 Å. for both  $H_2/O_2$  flames shown in Figure 4 indicated that the value of  $p_{OH}$  was approximately the same in both cases. It should not be too surprising that  $p_{OH}$  is the same in the outer cones of both flames, because there must be considerable entrainment of air in the turbulent flames produced over total consumption atomizer-burners. The OH intensity measurements were performed with the flame masked by a flat black baffle with an opening of approximately 2 mm. by 3 mm. The meter reading for the "fuel-rich" flame was approximately twice that of the "stoichiometric" flame, as would be expected for two flames at the same temperature, with the same  $p_{OH}$ , and a radius ratio of 2 to 1.

Figure 4 also shows that the theory is quite adequate in predicting the signal-to-noise ratios for the various flames. All the experimental points were shifted along the  $\log (i/\Delta i_T k_C)$  axis by the same factor, and the experimental points for each of the flames agree fairly well with their respective theoretical curves. Therefore the measured signal-to-noise ratios of the various flames must be related to each other in the same way as the theoretical signal-to-noise ratios. For

example, for  $\log P_T = -6$ , the theoretical values of  $\log (i/\Delta i_T k_c)$  for  $H_2/\text{air}$ ,  $H_2/O_2$  (curve 1), and  $C_2H_2/O_2$  are 12.3, 12.5, and 12.0, respectively, while the experimental values are 12.1, 12.6, and 11.9, respectively, i.e., the theoretical values of the three flames are in the ratio of 1.02/1.04/1.00, while the experimental values are in the ratio of 1.02/1.06/1.00, approximately the same, within experimental error.

The theoretical curve for the "stoichiometric"  $H_2/O_2$  flame (curve 2) has been adjusted to account for the size difference. Because the region viewed by the spectrometric system is wider than the flame width, the signal should increase as the square of the flame radius in going from the "stoichiometric" to the "fuel-rich" flame. The "fuel-rich"  $H_2/O_2$  flame has a radius of 1 cm., the "stoichiometric"  $H_2/O_2$  flame has a radius of 0.5 cm., and, therefore, the size correction should be a factor of 4. There is also a small temperature difference between the two  $H_2/O_2$  flames. In the smaller flame the temperature must be averaged over almost the entire flame, while in the larger flame the temperature must be averaged over a smaller portion of the flame. (The smaller flame was approximately 4 cm. long, while the larger flame was approximately 8 cm. long.)

The excellent agreement of the theoretical and experimental analytical curves also demonstrates that the influence of species such as NaO and NaH must be negligibly small. The agreement of theory and experiment also indicates that, contrary to many statements to be found in the literature, the formation of the NaOH species in the flame gases is not negligible.

The essential correctness of the equation for optimum slit width for atomic emission flame spectrometry, equation [53], has been verified by measuring the noise as a function of slit width. The peak-to-peak noise was measured at several slit widths above and below the calculated optimum slit width. The peak-to-peak noise was multiplied by  $1/2\sqrt{2}$  to obtain root-mean-square noise, and the ratio of  $W$  to root-mean-square noise was plotted versus  $W$ . For a constant intensity source, the signal should be proportional to  $W$  (see equation [47]), and  $W/\text{noise}$  should be proportional to signal/noise.

In Figure 5 the unbroken line indicates the calculated variation of  $\log (W/\overline{\Delta i_T})$  as a function of  $W$  for a  $H_2/O_2$  flame. The value of  $W/\overline{\Delta i_T}$  is given by

$$\begin{aligned} W/\overline{\Delta i_T} = & W [ 2BMe_c \Delta f (i_d + \gamma T_f WH(A/F^2) I_{cs}) \\ & + (\gamma T_f WH(A/F^2) \overline{\Delta I_{cs}})^2 \Delta f ]^{-1/2} . \end{aligned} \quad [112]$$

The circles in Figure 5 indicate measured values of  $\log (W/\text{noise})$  for a  $H_2/O_2$  flame. The measured values of  $W/\text{noise}$  were shifted along the signal-to-noise axis to obtain overlap of the experimental and theoretical values in order to compare curve shapes. Agreement of theoretical and experimental values is adequate. The scattering of experimental points is due to the difficulty of measuring accurately the small values of noise. All noise measurements were made at 5800 Å.

The  $H_2/\text{air}$  and  $C_2H_2/O_2$  flames gave signal-to-noise ratio versus  $W$  plots similar to the  $H_2/O_2$  flame plot. A Moseley x-y recorder (Model 135, F. L. Moseley Co., Pasadena, California) was used for all noise measurements.

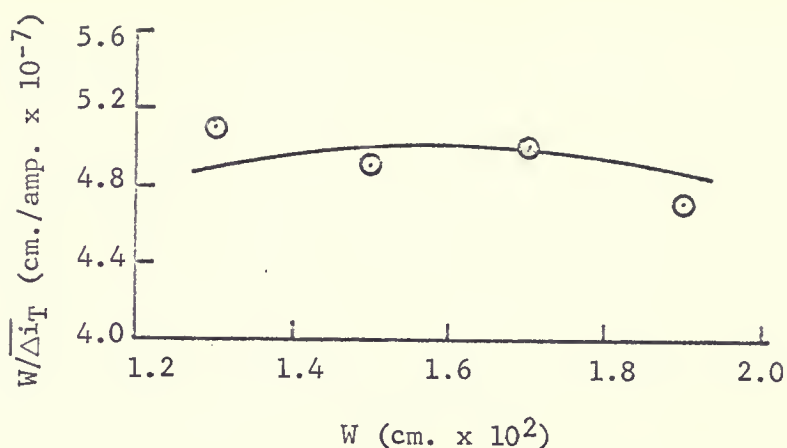


Figure 5. Calculated and Experimental Plots of Signal-to-Noise Ratio Versus Slit Width for Sodium in a Stoichiometric  $H_2/O_2$  Flame.

Because of the instrumental problems inherent in atomic absorption measurements of the alkali metals and because of the greater applicability of atomic emission flame spectrometry for the analysis of sodium, no experimental measurements of absorbance as a function of concentration (or  $P_T$ ) were made. However, because the theoretical atomic emission analytical curves agreed quite well with the experimental curves, it is highly probable that the theoretical and experimental atomic absorption analytical curves should also agree very well. The emission analytical curves depend directly upon  $N$ , as do the atomic absorption curves, and so the verification of the emission curves indirectly verifies the absorption curves.

## V. CONCLUSIONS

It is hoped that the work presented in this dissertation adequately demonstrates that both atomic emission and atomic absorption flame spectrometry can be treated quantitatively in a relatively simple manner. The equations discussed allow one to predict the effects of variation of instrumental slit width, the effects of compound formation and ionization in the flame, and the effects of self-absorption of radiation. This quantitative treatment makes it possible to predict the shape of analytical curves and, therefore, to choose conditions so as to obtain linear analytical curves. It is also possible to calculate values of limits of detectability, signal, noise, and signal-to-noise ratios for any instrumental setup.

Information on optimum experimental conditions for atomic emission and atomic absorption flame spectrometric analysis of any spectral line of any atom of any compound introduced into any flame and measured using any experimental setup could be presented in the form of graphs such as those in Figures 2 and 3. With accompanying data on optimum slit widths and limits of detectability for particular instruments, this information should be extremely valuable to many analysts using flame spectrometry who are not necessarily specialists in the field.

Enough data are presently available that a treatment such as has been presented in this paper for sodium could be applied to many elements of interest in flame spectrometry. Preliminary calculations have already

been carried out on Li, K, and Mg. The results of these calculations will be tested experimentally and presented at a later time. The quantitative approach presented in this paper certainly would seem to be a faster and surer method of obtaining optimum conditions than the trial-and-error methods presently employed.

It should be noted that the essential agreement with experiment of the theory presented in this paper should be good indirect evidence for the existence of chemical and thermal equilibrium in the flame, because equilibrium was assumed in the development of the theory. The theory of atomic emission flame spectrometry presented in this paper could also be extended to situations in which the excitation of radiation is non-thermal, e.g., excitation by chemiluminescence, by substitution of the proper expression for  $I$  in equation [76]. In fact, the general approach discussed in this paper could be extended, with good purpose, to many other areas of spectrometry. The case of the d.c. arc source is only one example of an area which could benefit greatly by being subjected to the quantitative approach presented in this dissertation.



## APPENDICES

## APPENDIX A

### Derivation of Current-Intensity Expression

The output signal of a photodetector, i.e., anodic current, in amperes, as a result of monochromatic radiation (spectral line half-width is assumed to be much narrower than the spectral slit width,  $s$ ) incident on the entrance slit of the monochromator, can be derived by consideration of entrance optics, monochromator optics, and the detector sensitivity. If the total (integrated) intensity of a spectral line is denoted as  $I$  and has units of  $\text{watts/cm}^2$  of source  $\cdot$  steradian, then the total power of radiation reaching the monochromator entrance slit as a result of this spectral line is given by

$$P_{\text{entrance}} =$$

$$I \cdot (\text{area of source}) \cdot (\text{solid angle viewed by monochromator}). \quad [113]$$

If the monochromator entrance slit is fully and uniformly illuminated by the radiation from the actual source, then the slit acts as the effective source, and so the area of the source is given by the area of the slit. The solid angle viewed by the monochromator is given by  $A$ , the effective aperture of the monochromator, divided by  $F^2$ , the square of the focal length of the collimator, as long as the effective aperture is fully illuminated.

Because of reflection and absorption losses within the monochromator, only a fraction  $T_f$  of the radiant power reaches the exit

slit. If the exit slit is equal to or slightly larger than the entrance slit, then the total power of radiation at the exit slit is

$$P_{\text{exit}} = P_{\text{entrance}} \cdot T_f \text{ watts} . \quad [114]$$

Using the detector sensitivity factor  $\gamma$  in amperes output at the anode per watt of radiation incident on the photocathode, the output current,  $i$ , from the phototube can be found, i.e.,

$$i = P_{\text{exit}} \gamma \text{ amperes} . \quad [115]$$

The output current of a photodetector in amperes as a result of polychromatic or continuous rather than monochromatic radiation incident on the monochromator entrance slit can be derived in a manner similar to the above case. However, in this particular case an additional factor must be included, namely the spectral slit width,  $s$ , of the monochromator. This is a result of the intensity of a continuum,  $I_c$ , being expressed as watts/cm.<sup>2</sup> of source  $\cdot$  ster.  $\cdot$  wavelength interval, and so in this case the total power of radiation reaching the monochromator exit slit as a result of a continuum being incident on the entrance slit is given by

$$P_{\text{exit}} = I_c \cdot (\text{area of source}) \cdot (\text{solid angle viewed by monochromator}) \cdot (\text{spectral slit width}) \cdot T_f \text{ watts} , \quad [116]$$

where the spectral slit width,  $s$ , is the wavelength interval passing through the exit slit for any particular wavelength setting. The current,  $i_c$ , due to the continuum can then be found by introducing equation [116] into equation [115].

The root-mean-square anodic noise current in amperes,  $\overline{\Delta i_c}$ , i.e., noise current at the anode of the phototube, is due to fluctuation in the intensity,  $\overline{\Delta I_c}$ , of continuous background radiation. Because  $\overline{\Delta I_c}$  is the root-mean-square fluctuation in the continuum, it has units of watts/cm.<sup>2</sup> of source  $\cdot$  ster.  $\cdot$  wavelength interval  $\cdot$  sec.<sup>-1/2</sup>. The last unit arises because the noise is a root-mean-square noise. In this case the root-mean-square fluctuation of radiant power,  $\overline{\Delta P_{exit}}$ , reaching the monochromator exit slit as a result of a fluctuating continuum intensity incident on the entrance slit is given by an equation identical to equation [116] except for the inclusion of the  $(\Delta f)^{1/2}$  factor, i.e.,

$$\overline{\Delta P_{exit}} = \overline{\Delta I_c} \cdot (\text{area of source}) \cdot (\text{solid angle viewed by monochromator}) \cdot (\text{spectral slit width}) \cdot T_f \cdot (\Delta f)^{1/2} \text{ watts}, \quad [117]$$

where  $\Delta f$  is the frequency response band width of the amplifier-recorder circuit. Both flame noise and phototube noise are assumed to be white and equally distributed over  $\Delta f$ .

Using the photosensitivity factor,  $\gamma$ , the root-mean-square anodic fluctuation current can be found, i.e.,

$$\overline{\Delta i_c} = \gamma \overline{\Delta P_{exit}}. \quad [118]$$

The linear relationship between the root-mean-square anodic noise current  $\overline{\Delta i_c}$  and the square root of the frequency response band width of the detection system has been considered by Goldman (19).

If the root-mean-square noise current is due to fluctuation of monochromatic radiation, an equation for  $\overline{\Delta P_{exit}}$  similar to equation [117] results, except that the spectral slit width is not included in the expression.

## APPENDIX B

### Optimization of Slit Width

Equation [16] can be squared and rewritten as shown below:

$$N_m^2 = \frac{C_1^2}{W^2} \left[ C_2 \left\{ i_d + C_3 I_c W (s_c + R_d W) \right\} + C_3^2 \overline{\Delta I_c}^2 (s_c + R_d W)^2 W^2 \right], \quad [119]$$

where  $s = s_m + s_c = R_d W + s_c$  is used, and where

$$C_1 = \frac{B \pi 10^7 B_T e^{E_u/kT} (\Delta f)^{1/2}}{\gamma T_f H(A/F^2) h \nu_o g_u A_t},$$

$$C_2 = 2e_c B M,$$

and

$$C_3 = \gamma T_f H(A/F^2).$$

Since for the positive root, minimization of  $N_m^2$  will occur at the same value as that of  $N_m$ , the above expression can be differentiated to give

$$2N_m \frac{dN_m}{dW} = C_1^2 \left[ -\frac{2C_2 i_d}{W^3} - \frac{C_2 C_3 s_c I_c}{W^2} + 2C_3^2 \overline{\Delta I_c}^2 s_c R_d + 2C_3^2 \overline{\Delta I_c}^2 R_d^2 W \right]. \quad [120]$$

Simplifying and equating to zero gives the optimum slit width equation

$$0 = 2(C_3 \overline{\Delta I_c} R_d)^2 W_0^4 + 2(C_3 \overline{\Delta I_c})^2 s_c R_d W_0^3 - C_2 C_3 I_c s_c W_0 - 2C_2 i_d. \quad [121]$$

Substituting for  $C_2$  and  $C_3$  gives equation [17].

If  $s_c \ll R_d W$ , then the  $N_m^2$  equation becomes

$$N_m^2 = \frac{C_1^2}{W^2} \left[ C_2 i_d + C_2 C_3 I_c R_d W^2 + C_3^2 \overline{\Delta I_c}^2 R_d^2 W^2 \right]. \quad [122]$$

Differentiating and setting equal to zero gives

$$0 = 2C_3^2 \overline{\Delta I_c}^2 R_d^2 W_o - \frac{2C_2 i_d}{W_o^3}, \quad [123]$$

which gives equation [18] when substitution is made for  $C_2$  and  $C_3$ .



## APPENDIX C

### The Shape of Spectral Lines and the Effect of Source Line Width

When the broadening of a spectral line (31) is due to contributions from a Gaussian shape, i.e., the Doppler effect, and from an independent shape, i.e., the damping effect due to natural damping and other damping effects, then (if the pressure shift due to collisional effects is small) the resulting atomic absorption coefficient as a function of frequency can be expressed by

$$k_{\nu}/k_0^* = \frac{a}{\pi} \int_{-\infty}^{+\infty} \frac{e^{-y^2} dy}{a^2 + (\nu - y)^2} , \quad [124]$$

where

$$y = (2\Delta/\Delta\nu_D) \sqrt{\ln 2} , \quad [125]$$

$$\nu = \frac{2(\nu - \nu_0)}{\Delta\nu_D} \sqrt{\ln 2} , \quad [126]$$

$$a = \frac{\Delta\nu_N + \Delta\nu_L + \Delta\nu_H}{\Delta\nu_D} \sqrt{\ln 2} . \quad [127]$$

The parameters  $k_{\nu}$  and  $k_0^*$  are, respectively, the atomic absorption coefficients at frequencies  $\nu$  and  $\nu_0$ , where  $\nu_0$  is the peak of the absorption line. The terms  $\Delta\nu_N$ ,  $\Delta\nu_L$ ,  $\Delta\nu_D$ , and  $\Delta\nu_H$  are, respectively, the half widths in  $\text{sec.}^{-1}$  of the absorption line due to natural, Lorentz (due to collisions of absorbing species with foreign atoms, molecules

of particles), Doppler, and Holtsmark (due to collisions of absorbing species with other similar species) broadening. The term  $\nu - \nu_0$  represents the frequency distance from the center of the line, and  $\Delta$  represents a variable distance from the point  $\nu - \nu_0$ . The term  $a$  is called the damping constant and indicates the relative contribution to the broadening of a spectral line by the damping factors (natural, Lorentz, and Holtsmark broadening).

The term on the right of equation [124] is the correction factor  $\delta$  (or  $\delta_\nu$ ) discussed in the body of the paper (equation [41]). The term  $k^0$  (or  $k_m^0$ ) used in the body of the paper is  $k_\nu$  at  $\nu = \nu_0$ , and  $\delta$  is  $(a/\pi) \int_{-\infty}^{+\infty} \frac{e^{-y^2} dy}{a^2 + (\nu - y)^2}$  at  $\nu = \nu_0$ . Thus

$$k^0 = k_0^* \delta, \quad [128]$$

where

$$k_0^* = \frac{2 \sqrt{\ln 2} \lambda_0^2}{\Delta \nu_D \sqrt{\pi} 8\pi} \frac{g_u}{g_0} N A_t. \quad [129]$$

Likewise  $\delta_\nu$  is the value of  $(a/\pi) \int_{-\infty}^{+\infty} \frac{e^{-y^2} dy}{a^2 + (\nu - y)^2}$  at some frequency  $\nu$  different from  $\nu_0$ , and

$$k_\nu = k_0^* \delta_\nu, \quad [130]$$

or, from equation [128]

$$k_\nu = k^0 \delta_\nu / \delta. \quad [131]$$

The integration in equation [124] is taken over the entire absorption line. The integral cannot be simply expressed and so must be evaluated by means of a suitable series or by numerical integration.

Poesner (33) has summarized the methods used for evaluating the right side of equation [124] and gives a complete table of values of  $k_V/k_O^*$  (or  $\delta_V$ ) as a function of  $v$  and  $\underline{a}$  values. In Poesner's tables the terms  $H(a, kw)$ ,  $H(a, 0)$  and  $k$  correspond respectively, to  $\delta_V$ ,  $\delta$ , and  $(V - V_O)/\Delta V_D$  in the nomenclature used in this paper.

The values of  $v$  and  $\underline{a}$  depend on the evaluation of  $\Delta V_D$ ,  $\Delta V_L$ ,  $\Delta V_N$ , and  $\Delta V_H$ . The expression for  $\Delta V_D$  has been given in the body of the paper (equation [45]). According to Mitchell and Zemansky (31) the Lorentz half width,  $\Delta V_L$ , is given by

$$\Delta V_L = Z_L/\pi = (2/\pi)\sigma_L^2 N_f [2\pi RT(1/M_a + 1/M_f)]^{1/2}, \quad [132]$$

where  $Z_L$  is the number of broadening collisions per second per absorbing atom,  $\sigma_L$  is the effective cross section for Lorentz broadening, in  $\text{cm}^2$ ,  $N_f$  is the number of foreign gas particles/ $\text{cm}^3$ , and  $M_f$  is the effective molecular weight of the foreign gas molecules. Assuming that the species in a flame are essentially an ideal gas, i.e.,  $P_f = \text{pressure of foreign particles} = kN_f T$ , where  $k$  is the Boltzmann constant, then  $N_f$  is given by

$$N_f = P_f/kT = 9.74 \times 10^{18} P_f/T, \quad [133]$$

if the value of  $k$  is substituted and if  $P_f$  is in mm. pressure. Substituting  $N_f$  into equation [132] and evaluating all constants gives

$$\Delta V_L = 1.38 \times 10^{23} \sigma_L^2 P_f [(1/T)(1/M_a + 1/M_f)]^{1/2}. \quad [134]$$

Hinnov and Kohn (22) have evaluated a number of  $\sigma_L$  and  $\underline{a}$  values for several spectral lines of a number of atoms.

Holtzmark broadening is due to collisions between atoms of the same kind, and can be treated in the same manner as the Lorentz broadening, i.e., replacing  $Z_L$  by  $Z_H$ ,  $\Delta\nu_L$  by  $\Delta\nu_H$ ,  $\sigma_L^2$  by  $\sigma_H^2$ ,  $P_f$  by  $P_a$ ,  $N_f$  by  $N$ , and  $M_f$  by  $M_a$ . If this is done the Holtzmark half width is given (31) by

$$\Delta\nu_H = Z_H/\pi = (2/\pi)\sigma_H^2 N [2\pi RT(1/M_a + 1/M_a)]^{1/2}, \quad [135]$$

and so

$$\Delta\nu_H = 2.08 \times 10^{23} \sigma_H^2 N [(1/M_a)T]^{1/2}. \quad [136]$$

The natural broadening half width is given (31) by

$$\Delta\nu_N = 1/2\pi\tau = A_t/2\pi, \quad [137]$$

where  $\tau$  is the lifetime of the excited state in seconds, and  $A_t$  is the transition probability in  $\text{sec}^{-1}$  of the spontaneous emission process.

In the above discussion and equations it was assumed that the spectral lines were Gaussian in shape. However, in many experiments spectral lines will show evidence of being asymmetrical and of being shifted towards the red region. Therefore, the value of the measured atomic absorption coefficient will be somewhat less than the value at  $\nu = \nu_0$ , the absorption line peak. In most cases the deviation in the atomic absorption coefficient at  $\nu = \nu_0$  from the calculated value if shift and asymmetry were negligible is smaller than the errors in the evaluation of the factors in the expression for  $k^0$  (39). Also the broadening of a spectral line by the hyperfine structure results in an even smaller error. Thus the factor of shift and asymmetry can usually be neglected. Mitchell and Zemansky (31) discuss the evaluation of the

pressure shift of spectral lines of Hg and Na. For a variety of foreign gases the pressure shift was seldom greater than 20 per cent of the Lorentz half-width for both Na and Hg. For all calculations performed in this paper the effects of pressure shift and asymmetry have been assumed negligible.

The effect of the finite width of the hollow cathode line has also been neglected, and it is interesting to investigate the magnitude of the error that this might introduce. Table 8 shows the per cent error in  $N$  and  $A^0$  values as a function of the product  $k^0L$  and of the ratio  $\Delta V_E/\Delta V_D$ , in the emission line width to the absorption line width. This ratio has been designated  $\alpha$ . The data under  $\alpha$  equals 0.25 and 0.75 were taken from Vidale (39). The rest of the table was calculated from data given in Appendix D of Mitchell and Zemansky (31) on values of  $A_\alpha$  (where  $A_\alpha = 1 - (I/I^0)$ ) as a function of  $\alpha$  and  $k^0L$ . The per cent error in  $N$  was taken as 100 times one minus the ratio of  $A_\alpha$  at a given  $\alpha$  to  $A_\alpha$  at  $\alpha = 0$ , i.e.,

$$\text{per cent error} = \left( 1 - \frac{A_\alpha}{A_{\alpha=0}} \right) 100 . \quad [138]$$

Table 8 shows that the error in  $N$  increases rapidly as  $\alpha$  increases, but with the precautions usually taken in atomic absorption flame spectrometry,  $\alpha$  should not exceed 0.5. For Na 5890 Å. at 2700°K. at the limit of detectability listed in Table 4,  $k_m^0L$  is only 0.004. Hence the error introduced by neglecting the finite width of source line should be well under 10 per cent.

TABLE 8

PER CENT ERROR IN N AND ABSORBANCE VALUES DUE TO FINITE WIDTH OF  
SOURCE EMISSION LINE AS COMPARED TO WIDTH OF ABSORPTION LINE

| $\alpha = \Delta\nu_E / \Delta\nu_D$ |     |      |      |      |     |     |
|--------------------------------------|-----|------|------|------|-----|-----|
| $k^o_L$                              | 0   | 0.25 | 0.50 | 0.75 | 1.0 | 2.0 |
| 0.00                                 | 0.0 | 0.0  | 0.0  | 0.0  | 0.0 | 0.0 |
| 0.25                                 | 0.0 | 3.0  | 10.0 | 20.7 | 30  | 57  |
| 0.50                                 | 0.0 | 3.0  | 10.5 | 21.2 | 31  | 58  |
| 1.0                                  | 0.0 | 3.0  | 12   | 21.7 | 33  | 62  |
| 1.5                                  | 0.0 |      | 12   |      | 36  | 66  |
| 2.0                                  | 0.0 |      | 12   |      | 38  | 68  |
| 3.0                                  | 0.0 |      | 14   |      | 42  | 72  |
| 4.0                                  | 0.0 |      | 15   |      | 47  | 76  |
| 4.5                                  | 0.0 |      | 16   |      | 49  | 78  |



## APPENDIX D

### Effects of Hyperfine Structure on Measured Absorbance

The effect of hyperfine structure on atomic absorption has been considered by Vidale (39). Hyperfine structure is due to the nuclear spin effect and isotope shift. Whether due to the occurrence of isotopes or to nuclear spin, the intensities and absorbances of the individual hyperfine components always occur in a certain ratio (31).

If the effect of isotopes alone is considered, then the ratio of line intensities of the source and absorbances due to atomic vapor is dependent only on the ratio of abundances.

$$I_1^0:I_2^0:I_3^0: \dots = k_1^0L:k_2^0L:k_3^0L: \dots = T_1:T_2:T_3: \dots, [139]$$

where  $T_i$  is the abundance of isotope  $i$ .

A single isotope may have a number of components due to the nuclear spin effect. In this case

$$I_1^0:I_2^0:I_3^0: \dots = k_1^0L:k_2^0L:k_3^0L: \dots = \eta_1:\eta_2:\eta_3: \dots, [140]$$

where the fraction  $\eta_i$  for component  $i$  is the ratio of the intensity of component  $i$  to the sum for the intensities of all the components due to nuclear spin, i.e.,

$$\eta_i = I_i^0 / \sum_{j=1}^n I_j^0 . \quad [141]$$

When both the isotope shift and the nuclear spin effect are considered, then

$$I_1^0 : I_2^0 : I_3^0 : \dots = k_1^0 L : k_2^0 L : k_3^0 L : \dots = \omega_1 : \omega_2 : \omega_3 : \dots , \quad [142]$$

where the fraction  $\omega_i$  for component  $i$  is given by

$$\omega_i = T_i \eta_i . \quad [143]$$

Thus one may write (31) for the value of the emitted intensity of a given component  $i$

$$I_i^0 = \omega_i (I_1^0 + I_2^0 + I_3^0 + \dots) = \omega_i I^0 , \quad [144]$$

where  $I^0$  is the total emitted intensity of a line from a source in which the spectral line includes hyperfine structure. Similarly the absorbance of a hyperfine component  $i$  is given by

$$k_i^0 L = \omega_i (k_1^0 L + k_2^0 L + k_3^0 L + \dots) = \omega_i k^0 L , \quad [145]$$

where  $k^0 L$  is the total absorption coefficient times the path length for the spectral line with the same hyperfine structure.

The transmitted intensity for a single hyperfine component is given by (from equation [23])

$$I_{t_i} = I_i^0 e^{-k_i^0 L} = \omega_i I^0 e^{-\omega_i k^0 L} , \quad [146]$$

where  $I_{t_i}$  is the transmitted intensity of component  $i$ . Because the total transmitted intensity  $I_t$  must equal the sum of the individual transmitted intensities (if the individual components are not resolved by the monochromator), i.e.,

$$I_t = I_{t_1} + I_{t_2} + I_{t_3} + \dots, \quad [147]$$

it follows that

$$I_t = I^0(\omega_1 e^{-\omega_1 k^0 L} + \omega_2 e^{-\omega_2 k^0 L} + \dots). \quad [148]$$

Expanding the exponential term one obtains

$$I_t = I^0[\omega_1(1 - \omega_1 k^0 L + \dots) + \omega_2(1 - \omega_2 k^0 L + \dots) + \dots], \quad [149]$$

$$I_t = I^0[\omega_1 - \omega_1^2 k^0 L + \dots + \omega_2 - \omega_2^2 k^0 L + \dots], \quad [150]$$

$$I_t = I^0[(\omega_1 + \omega_2 + \dots) - (\omega_1^2 + \omega_2^2 + \dots)k^0 L + \dots]. \quad [151]$$

Since  $\sum \omega_i = 1$ ,

$$I_t = I^0[1 - \sum \omega_i^2 k^0 L + \dots], \quad [152]$$

or  $I_t$  is given approximately by

$$I_t = I^0 e^{-\sum \omega_i^2 k^0 L}, \quad [153]$$

where the summation is taken over all nuclear spin components of all isotopic components of the spectral line in concern. By comparison with equation [24] it may be seen that the correction factor  $\rho$  is in this case  $\sum \omega_i^2$ .

In this derivation it has been assumed that the hyperfine structure components do not overlap appreciably. With this assumption  $\rho$  may be obtained for simple atoms without great difficulty. The evaluation of  $\sum \omega_i^2$  for Na 5890 Å. is illustrative of the procedure. The Na 5890 Å. line arises from a transition between the  $^2S_{1/2}$  ground state and the  $^2P_{3/2}$  excited state. Sodium has only one naturally occurring isotope

with a nuclear spin of  $3/2$  (5). The  $^2S_{1/2}$  level thus has two substates having  $F$  values of 2 or 1, while the  $^2P_{3/2}$  level has four substates having  $F$  values of 3, 2, 1, and 0. The hyperfine structure splitting constant of the  $^2S_{1/2}$  state is  $0.0591 \text{ cm.}^{-1}$  (27), and that of the  $^2P_{3/2}$  state is  $0.00066 \text{ cm.}^{-1}$  (36). The splitting between the levels of the upper state is therefore,  $0.00066 \text{ cm.}^{-1}$  between 0 and 1,  $0.00132 \text{ cm.}^{-1}$  between 1 and 2, and  $0.00198 \text{ cm.}^{-1}$  between 2 and 3. Applying the selection rule  $\Delta F = 0, \pm 1$  and obtaining the relative intensities of the hyperfine lines from the tables by White and Eliason (40), Table 9 is obtained.

Table 9 makes it clear that the assumption of no overlap of the hyperfine components is, in this case, not valid. The Doppler half width at  $2700^\circ\text{K.}$  is  $4.1 \times 10^9 \text{ sec.}^{-1}$  or  $0.13 \text{ cm.}^{-1}$ . Three of the components, whose relative intensities total to 85.7, lie within  $0.0020 \text{ cm.}^{-1}$  of each other, and the other three with a total relative intensity of 142.8, lie within  $0.0033 \text{ cm.}^{-1}$  of each other. The splitting within the two groups is so much smaller than the Doppler width ( $0.133 \text{ cm.}^{-1}$ ) as to be negligible. Thus the six components can be considered as two lines with an intensity ratio of 3:5 separated by  $0.058 \text{ cm.}^{-1}$ . Thus if the line centering around  $-0.0009 \text{ cm.}^{-1}$  (on the arbitrary scale of Table 9) is designated line 1, then  $\eta_1 = 3/8$ , and if the line centering around  $0.057 \text{ cm.}^{-1}$  is designated line 2, then  $\eta_2 = 5/8$ . Since the abundance is 1,  $\omega_1 = 3/8$ ,  $\omega_2 = 5/8$  and  $\Sigma \omega_i^2 = 0.53$ .

However, this factor is still too low because the appreciable overlap of the two lines has been neglected. For this case equation [148] should read (39)

TABLE 9  
HYPERFINE STRUCTURE COMPONENTS OF THE Na 5890 A. LINE

| Transition<br>upper to lower | Frequency shift (cm. <sup>-1</sup> )<br>relative to first<br>component | Relative<br>intensity |
|------------------------------|------------------------------------------------------------------------|-----------------------|
| 0-1                          | 0                                                                      | 14.3                  |
| 1-1                          | -0.0007                                                                | 35.7                  |
| 1-2                          | 0.0584                                                                 | 7.1                   |
| 2-1                          | -0.0020                                                                | 35.7                  |
| 2-2                          | 0.0571                                                                 | 35.7                  |
| 3-2                          | 0.0551                                                                 | 100                   |

$$I_t = I^0(\omega_1 e^{-\omega_1 k^0 L - \omega_2 k_v L} + \omega_2 e^{-\omega_2 k L - \omega_1 k_v L}) , \quad [154]$$

where  $k_v$  is the atomic absorption coefficient of component 1 or 2 at the peak frequency of component 2 or 1, respectively. In this case the displacement from the line center is  $0.058 \text{ cm}^{-1}$ . Following the procedure previously employed with equation [148] one obtains

$$I_t = I^0 [\omega_1 (1 - \omega_1 k^0 L - \omega_2 k_v L) + \omega_2 (1 - \omega_2 k^0 L - \omega_1 k_v L)] . \quad [155]$$

But  $k_v$  can be written in terms of  $k^0$  if the line is assumed symmetrical (33) (see Appendix C) such that  $k_v = (\delta_v / \delta) k^0$ . Values of  $\delta_v$  can be found from the tables given by Poesner (33). Thus

$$I_t = I^0 [\omega_1 - \omega_1^2 k^0 L - \omega_1 \omega_2 (\delta_v / \delta) k^0 L + \omega_2 - \omega_2^2 k^0 L - \omega_1 \omega_2 (\delta_v / \delta) k^0 L] , \quad [156]$$

$$I_t = I^0 [(\omega_1 + \omega_2) - (\omega_1^2 + \omega_2^2 + 2\omega_1 \omega_2 \delta_v / \delta) k^0 L] , \quad [157]$$

$$I_t = I^0 [1 - (\omega_1^2 + \omega_2^2 + 2\omega_1 \omega_2 \delta_v / \delta) k^0 L] , \quad [158]$$

$$I_t = I^0 e^{-(\Sigma \omega_i^2 + 2\omega_1 \omega_2 \delta_v / \delta) k^0 L} . \quad [159]$$

Thus it may be seen that the improved correction factor differs from 0.53 by the term  $2\omega_1 \omega_2 \delta_v / \delta$ . In this case  $\rho = \omega_1^2 + \omega_2^2 + 2\omega_1 \omega_2 \delta_v / \delta = 0.97$ .

Still further corrections may be necessary in the most exact work, but for the purpose of this paper the above value of  $\rho$  suffices.

For the case of the Cd 2288 A. line which has eight isotopes, several groupings of components would result. This would considerably complicate the above procedure given for the Na 5890 A. line which



contained only two groupings of components. Data for the isotope shifts in the hyperfine structure of the Cd 2288 Å. line were not readily available, and so the correction factor for hyperfine structure was not calculated. The value of  $\rho$  was taken as 1 in the calculations given in Table 4, and this value should be sufficiently accurate for the purpose of this paper.

## APPENDIX E

### Influence of Thermal Emission on $N_m$

In atomic absorption flame spectrometry, atoms with resonance lines at wavelengths longer than 3000 Å. emit appreciably due to thermal excitation. Therefore, the current due to the transmitted radiation when sample is present in the flame cell will also contain a contribution due to thermal emission. This contribution will be quite small for resonance lines below 3000 Å. and could be extremely large for resonance lines above 5000 Å. Therefore, in order to make accurate measurements of absorbance and concentration, the current due to thermal emission must be subtracted out from the total current due to the transmitted intensity from the source and the thermal emission.

The current due to thermal emission will depend greatly on the method of detection of the radiation. If a d.c. amplifier-readout system is used, the magnitude of the current due to thermal emission will be quite large. However, if an a.c. amplifier-readout system is used, the magnitude of the current due to thermal emission will depend greatly on the band width of the detection system as well as on the wavelength of the resonance line and the flame cell temperature. In the body of the paper it was assumed in all equations that thermal emission was corrected for. It is of considerable interest, however, to determine the magnitude of the effect of thermal emission on  $N_m$  for cases in which compensation is not made in the measurement procedure.

For the case in which a d.c. amplifier-readout system is used for detection of the radiation, and for which thermal emission is not compensated, the minimum detectable current difference (see equation [25]) is given by

$$[i^0 - (i_t + i_e)]_m = 2\overline{\Delta i}_T, \quad [160]$$

where  $i_e$  is the anodic current of the photodetector in amperes and is due to the constant thermal emission of the atoms in concern at the minimum detectable concentration,  $N_m$ , and all other terms are as previously defined. The current  $i_e$  is given by an equation similar to equation [27], namely,

$$i_e = \gamma T_f^{WH} (A/F^2) I_e, \quad [161]$$

where  $I_e$  is the intensity of thermal emission of the resonance line for the minimum detectable concentration  $N_m$  and is given by the following expression

$$I_e = (10^{-7}/4\pi) N_m L h \nu_0 A_t [g_u/B(T)] e^{-E_u/kT}, \quad [162]$$

where  $\nu_0$  is the frequency of the center of the absorption line in  $\text{sec.}^{-1}$ ,  $E_u$  is the excitation energy of the atom in e.v.,  $k$  is the Boltzmann constant in e.v./°K.,  $B(T)$  is the partition function of the atom and is given approximately by  $g_0$  for most atoms, and all other terms in the above equations are as previously defined.

For the case of a d.c. amplifier-readout system, the following equation for  $N_m$  results when  $i^0$  and  $i_t$  are substituted for in the manner described in Section III, and  $i_e$  is substituted for using equation [161].

$$N_m = \frac{8\pi B(T)}{LA_t g_u} \left[ \frac{I^o \sqrt{\ln 2} \lambda_o^2}{\sqrt{\pi} \Delta \nu_D} - \frac{10^{-7} h c e^{-E_u/kT}}{\lambda_o} \right]^{-1} .$$

$$\left[ \frac{2BMe_c I^o}{8T_f W_{HA}/F^2} + (\chi I^o)^2 + (\xi I_{cs})^2 \right] \Delta f \Bigg]^{1/2} . \quad [163]$$

The optimum slit width,  $W_o$ , can be obtained as described in Section III and is given by the same equation as previously described, namely, equation [43].

Equation [163] reduces to equation [42] if the thermal emission term  $10^{-7} (hc/\lambda_o) e^{-E_u/kT}$  is small, i.e., if thermal emission is negligible. For the case in which the resonance line is below 3000 Å. the contribution due to the thermal emission term is negligible for most flames but for the case in which the resonance line is above 5000 Å. the contribution due to thermal emission may be appreciable and may be even greater than the absorption term  $I^o \sqrt{\ln 2} \lambda_o^2 \delta \rho / \sqrt{\pi} \Delta \nu_D$ . The latter case is particularly true of the resonance lines of the alkali metals when excited in  $H_2/O_2$  or  $C_2H_2/O_2$  flames. Therefore, if the thermal emission signal is measured and subtracted from the signal due to the transmitted intensity and the thermal emission, then the value of  $N_m$  can be found by use of equation [42]. If thermal emission is not subtracted out in the measurement procedure, then the value of  $N_m$  must be found by use of equation [163]. In the latter situation it may be found that in some cases, particularly with the resonance lines of the alkali metals, sensitivity is lost or even that analysis by this method is impossible.

When using a d.c. amplifier-readout system, it is common practice and usually necessary to subtract out the current due to thermal emission. However, when using an a.c. amplifier-readout system many analysts neglect correction for thermal emission. The correction for thermal emission may be negligibly small or very large, being dependent on the temperature of the flame, the excitation energy of the resonance line, and the band width of the electronic system. In the paragraph below the effect of thermal emission on the limiting detectable concentration will be calculated when using an a.c. amplifier-rectifier-readout system.

For the case of using an a.c. amplifier-rectifier-readout system for the detection system, the minimum detectable difference current (see equation [160]) will be given by

$$[i^0 - (i_t + \overline{\Delta i_e})]_m = 2\overline{\Delta i_T} . \quad [164]$$

The term  $\overline{\Delta i_e}$  represents the photodetector output due to the rectified signal which results from the thermal emission flicker over the amplifier band width frequency,  $\Delta f$ , at the wavelength setting of the monochromator, and it is given by

$$\overline{\Delta i_e} = \gamma T_f W H (A/F^2) \overline{\Delta I_e} (\Delta f)^{1/2} , \quad [165]$$

where  $\overline{\Delta I_e}$  is the fluctuation in the intensity of the thermal emission. The value of  $N_m$  in this case can be obtained when  $i^0$  and  $i_t$  are substituted for as described in Section III,  $\overline{\Delta i_e}$  is substituted for using equation [165] evaluated for the minimum detectable concentration, and  $\overline{\Delta I_e} = \psi I_e$  where  $I_e$  is the thermal emission intensity for the minimum detectable concentration as expressed by equation [162]. If this is done, then  $N_m$  is given by

$$N_m = \frac{8\pi B(T)}{LA_t g_u} \left[ \frac{I^0 \sqrt{\ln 2} \lambda_o^2 \mathcal{S}_p}{\sqrt{\pi} \Delta \nu_D} - \frac{10^{-7} hc \psi(\Delta f)^{1/2} e^{-E_u/kT}}{\lambda_o} \right]^{-1}$$

$$\left[ \left\{ \frac{2BMe_c I^0}{\delta T_{fWHA}/F^2} + (\chi I^0)^2 + (\xi I_{cs})^2 \right\} \Delta f \right]^{1/2} . \quad [166]$$

Differentiating  $N_m$  with respect to  $W$ , setting the result equal to zero, and solving for  $W_o$  gives the same equation for the optimum slit width as found in Section III, namely, equation [43].

Equation [166] reduces to equation [42] if the thermal emission term  $10^{-7} (hc/\lambda_o) \psi(\Delta f)^{1/2} e^{-E_u/kT}$  is small compared with the absorption term  $I^0 \sqrt{\ln 2} \lambda_o^2 \mathcal{S}_p / \sqrt{\pi} \Delta \nu_D$ . For the case of atoms with resonance lines in the u.v., the thermal emission term will only become significant when using amplifiers responding to a range of frequencies for the detector system for the measurement of resonance lines in the visible region (wavelengths longer than 4000 Å.) when using high temperature flames ( $H_2/O_2$ ,  $C_2H_2/O_2$ , etc.). Therefore, if the thermal emission is measured and subtracted from the transmitted intensity plus thermal emission signal, then the value of  $N_m$  can be calculated by the use of equation [42]. If the thermal emission is not subtracted out in the measurement procedure, then the value of  $N_m$  must be found by the use of equation [166].

#### Influence of Atomic Fluorescence on $N_m$

All atoms are capable of re-emitting the absorbed energy from the resonance source (2,31,34). At the 1962 Spectroscopy Colloquium, Alkemade (2) discussed the fluorescence process, particularly with regard



to the Na 5890, 5896 Å. doublet. For the case of the Na doublet, Alkemade found that the re-emission of radiation due to the absorbed radiation was only of the order of 0.6 per cent of the thermal emission. For atoms with resonance lines in the visible, the fraction of fluorescent radiation compared to thermal radiation should be negligible as in the case of Na. Because the intensity of the fluorescent radiation depends on the intensity of the resonance line source as well as on the efficiency of converting the absorbed radiation to fluorescent radiation and on the fraction of radiation absorbed (2,45), the fluorescent intensity may not always be small compared to the intensity of radiation from the source transmitted by the flame. Work performed in this laboratory (44) has shown that Zn, Cd, and Hg fluoresce appreciably at low concentrations when excited by resonance lamps. In fact the fluorescence is sufficiently great that atomic fluorescence has been applied as a means of analysis for these elements.

In cases where fluorescence is important it would be necessary to subtract out the constant contribution due to fluorescence in the same manner as done for thermal emission, i.e., equation [25] should now be written

$$[i^0 - (i_t + i_e + i_f)]_m = 2\overline{\Delta i_T}, \quad [167]$$

where  $i_f$  is the anodic current of the photodetector in amperes due only to the fluorescent radiation. If the resonance source is placed at right angles to the optical axis of the monochromator and is arranged with the same geometry of entrance optics prior to the flame cell, then the terms  $i_e + i_f$  can be measured by introducing sample into the flame and measuring the anodic phototube current due to the sample.

Influence of Scattering of Incident Radiation by  
Particles in the Flame Gases

Small particles, such as unevaporated solvent droplets, will result in scattering of the incident radiation. This problem will particularly exist when using total-consumption atomizer burners where sample introduction efficiency may be less than complete (42). If scattering were significant, then equations [167] and [31] would have to be changed as follows

$$[i^0 - (i + i_e + i_f - i_s)]_m = 2\overline{\Delta i}_T, \quad [168]$$

$$\overline{\Delta i}_T = [\overline{\Delta i}_p^2 + \overline{\Delta i}^2 + \overline{\Delta i}_c^2 + \overline{\Delta i}_s^2]^{1/2}, \quad [169]$$

where  $i_s$  and  $\overline{\Delta i}_s$  are the photodetector signal due to incident light scattering and the root-mean-square noise signal in amperes due to fluctuation in the scattered signal, respectively.

Winefordner, Mansfield, and Vickers (42) found the fraction of scattered radiation to be as much as 2 per cent ( $i_s = 0.02 i^0$ ) at a solution (aqueous) flow rate of 2 cm.<sup>3</sup> per min. and 5.5 per cent ( $i_s = 0.055 i^0$ ) at a solution flow rate of 3 cm.<sup>3</sup> per min., when using total consumption atomizers. Therefore, when making atomic absorption measurements of dilute solutions, it is important to determine the extent of scattering and to correct the photodetector signal. Of course, the extent of scattering is much less when using low solution flow rates, organic solvents, or chamber-type atomizers. The noise signal due to scattering,  $\overline{\Delta i}_s$ , should be considerably less than  $\overline{\Delta i}^0$  in many practical cases and will not be considered in general. However, the analyst should be cautioned that  $\overline{\Delta i}_s$  may in some cases be significant.

## APPENDIX F

### Effect of Common Atom on NaCl Dissociation--Introduction of NaCl in an HCl Solution into the Flame

Consider the introduction into the flame of NaCl in the presence of the mineral acid HCl. The important equilibria are:



$$K_1 = \frac{P_{\text{Na}}P_{\text{Cl}}}{P_{\text{NaCl}}}, \quad [170]$$



$$K_H = \frac{P_{\text{H}}P_{\text{Cl}}}{P_{\text{HCl}}}, \quad [171]$$



$$K_3 = \frac{P_{\text{Na}}P_{\text{OH}}}{P_{\text{NaOH}}}. \quad [172]$$

To determine the effect of the common atom, Cl, the worst possible case will be considered, i.e., the case in which the HCl introduced into the flame is completely dissociated. (Actually the fraction of HCl dissociated is given by  $K_H/(K_H + p_H)$ , which will generally be greater than 0.9 for most analytical flames.) Thus  $p_{\text{Cl}} \approx P_{\text{Cl}}$ , where  $P_{\text{Cl}}$  is the total pressure of HCl introduced into the flame.

In order to obtain the full effect of the common atom effect, it will be assumed that the ionization of Na atoms is negligible.

Therefore

$$P_T = P_{Na} + P_{NaCl} + P_{NaOH} , \quad [173]$$

and

$$P_T = P_{Na}(1 + P_{Cl}/K_1 + P_{OH}/K_3) , \quad [174]$$

and so

$$P_{Na} = \frac{P_T}{(1 + P_{Cl}/K_1 + P_{OH}/K_3)} . \quad [175]$$

The influence of HCl on the value of  $p_{Na}$  is only significant when the following condition is either met or exceeded:

$$P_{Cl}/K_1 = 0.1(1 + P_{OH}/K_3) , \quad [176]$$

and

$$P_{Cl} = 0.1K_1(1 + P_{OH}/K_3) . \quad [177]$$

For a  $H_2$ /air flame at  $2000^\circ K.$ ,  $K_1 = 9.1 \times 10^{-5}$ ,  $K_3 = 4.1 \times 10^{-5}$ , and  $P_{OH} = 10^{-3}$  atm., and so  $P_{Cl}$  is  $2.2 \times 10^{-4}$  atm. Using equation [58] and the atomizer conditions given in Section IV, it can be shown that this pressure of HCl corresponds to a solution concentration of HCl,  $C_{HCl}$ , of 0.15 M. Similarly for a  $H_2/O_2$  flame at  $2600^\circ K.$ ,  $K_1 = 1.3 \times 10^{-2}$ ,  $K_3 = 1.3 \times 10^{-2}$ ,  $P_{OH} = 0.05$  atm., and so  $P_{Cl} = 6.3 \times 10^{-3}$  atm. and  $C_{HCl} = 3.2$  M. For a  $C_2H_2/O_2$  flame at  $2800^\circ K.$ ,  $K_1 = 4.2 \times 10^{-2}$ ,  $K_3 = 2.9 \times 10^{-2}$ ,  $P_{OH} = 0.2$  atm., and so  $P_{Cl} = 3.2 \times 10^{-2}$  atm., and  $C_{HCl} = 14$  M, an impossibly high solution concentration.

Thus when using the  $H_2$ /air,  $H_2/O_2$ , and  $C_2H_2/O_2$  flames, the concentration of hydrochloric acid in the NaCl solutions used for aspiration must exceed 0.15 M, 3.2 M, and 14 M, respectively, before a 10 per cent change in  $p_{Na}$  results. Because of the deleterious effects of

acids on the aspiration characteristics, it is seldom advisable for the analyst to use mineral acids of any kind at concentrations greater than 0.1 M. At this concentration, even in the case of complete dissociation of the introduced HCl, the effect of the common atom is generally negligible.

## APPENDIX G

### Integrated Intensity of a Spectral Line

A brief derivation of the intensity of a spectral line has been given by Alkemade (1) from a consideration of curves of growth and black body theory. A fuller derivation of the intensity of spectral lines is given here from a consideration of black body theory. In this derivation it is assumed that the absorbing and emitting atoms are uniformly distributed in the flame, and that the absorption power of the considered absorption line is independent of the presence of other lines (1).

The integrated intensity,  $I$ , of a spectral line emitted by atoms in thermal equilibrium in a homogeneous source (an approximation for flames used in flame spectrometry) can be expressed according to Kirchhoff's Law (7,10,22) as

$$I = \int I_{\nu}^B A_{\nu} d\nu = I_{\nu_0}^B \int A_{\nu} d\nu = I_{\nu_0}^B A_T, \quad [178]$$

where the integral is over the entire spectral line,  $I_{\nu}^B$  is the intensity of a black body radiator at frequency  $\nu$ ,  $I_{\nu_0}^B$  is the intensity of a black body radiator at frequency  $\nu_0$ , the line center,  $A_{\nu}$  is the atomic absorptivity of the source at frequency  $\nu$  and  $A_T$  is the total absorption of the spectral line. Because the value of  $I_{\nu}^B$  does not vary much over the width of the spectral line,  $I_{\nu}^B$  can be removed from within the integral and set equal to  $I_{\nu_0}^B$ , the black body intensity at frequency  $\nu_0$ . The term  $I_{\nu_0}^B$  can be evaluated (15,32) by Planck's equation, namely,



$$I_{\nu_o}^B = \frac{2h\nu_o^3}{10^7 c^2} \left( \frac{1}{e^{h\nu_o/kT} - 1} \right), \quad [179]$$

where  $I_{\nu_o}^B$  is in watts/cm.<sup>2</sup> ster. For the case of analytical flames and spectral lines of importance in atomic emission flame spectrometry, the term  $\exp(h\nu_o/kT)$  is much greater than one, and so  $I_{\nu_o}^B$  can be given with sufficient accuracy by the well known Wien's Law, namely,

$$I_{\nu_o}^B = \frac{2h\nu_o^3}{10^7 c^2} e^{-h\nu_o/kT}, \quad [180]$$

where  $C$  is the speed of light in cm./sec.,  $k$  is the Boltzmann constant in ergs/°K., and  $h$  is Planck's constant in ergs-sec.

From equation [178] it may be seen that the intensity of a spectral line is equal to the black body intensity times the total absorption factor,  $A_T$ . Only if the flame radiates as a black body at the flame temperature  $T$ , in the region of the spectral line, will the total absorption factor be unity. The parameter  $A_T$  is then a factor to correct for deviation of the flame from true black body character. The total absorption factor  $A_T$  is defined (4,22,31,32,38) according to the equation given below, i.e.,

$$A_T = \int_{\text{line}} (1 - e^{-k_\nu L}) d\nu, \quad [181]$$

where the integration is over the entire spectral line,  $k_\nu$  is the atomic absorption coefficient in cm.<sup>-1</sup> at frequency  $\nu$ , and  $L$  is the flame diameter.

The evaluation of  $k_\nu$  is given in several books (31,38) and papers (22,23,24) and will not be given here. Several authors (4,7,31,38)

have evaluated the total absorption factor,  $A_T$ , for various situations. Only the final results will be given here. If a spectral line is broadened only by Doppler broadening, and if  $k_0^*L$  is small, i.e., the absorber is a dilute gas, then it can be shown (38) that

$$A_T = \frac{\Delta\nu_D}{2\sqrt{\ln 2}} k_0^* L \pi^{1/2} \left\{ 1 - \frac{k_0^* L}{2! \sqrt{2}} + \frac{(k_0^* L)^2}{3! \sqrt{3}} - \frac{(k_0^* L)^3}{4! \sqrt{4}} + \dots \right\}, [182]$$

and if  $k_0^*L$  is very small, the limiting equation is

$$A_T = \frac{\Delta\nu_D}{2\sqrt{\ln 2}} k_0^* L \pi^{1/2}, [183]$$

where  $\Delta\nu_D$  is the Doppler half-intensity width in  $\text{sec.}^{-1}$  and  $k_0^*$  is the maximum atomic absorption coefficient in  $\text{cm.}^{-1}$  for a pure Doppler broadened line. The term  $k_0^*$  is given (31) by

$$k_0^* = \frac{2}{\Delta\nu_D} \left( \frac{\ln 2}{\pi} \right)^{1/2} \frac{\lambda_0^2}{8\pi} \frac{g_u}{B(T)} N A_t, [184]$$

where all terms have been previously defined. Therefore the value of  $A_T$  for the limiting case of very small  $k_0^*L$  is

$$A_T = \frac{\lambda_0^2}{8\pi} \frac{g_u}{B(T)} N A_t L. [185]$$

The above equation also results for the case of pure damping broadening (7,38), if  $k_0^*L$  is very small. However, if  $k_0^*L$  is large, and if the line broadening is entirely due to damping effects, then it can be shown (23,24,38) that

$$A_T = \frac{2\Delta\nu_D}{2\sqrt{\ln 2}} \left( \frac{k_0^* L a}{\pi^{1/2}} \right)^{1/2} \pi^{1/2}, [186]$$

and substituting for  $k_0^*$  gives

$$A_T = \left( \frac{\lambda_o^2}{4\pi} \frac{\Delta \mathcal{V}_D}{\sqrt{\ln 2}} \frac{g_u}{B(T)} a NA_t L \right)^{1/2} . \quad [187]$$

If the above values of  $A_T$  and the Wien expression for  $I_{\mathcal{V}_O}^B$  are substituted into the Kirchoff equation, then the integrated intensity expressions given in the text of the paper result. For small  $k_O^*L$  values,

$$I = \frac{h\mathcal{V}_O}{10^7 4\pi} \frac{g_u}{B(T)} NA_t L e^{-E_u/kT} , \quad [77]$$

in units of watts/cm.<sup>2</sup> ster. For large  $k_O^*L$  values

$$I = \frac{h\mathcal{V}_O^2}{10^7 c} e^{-E_u/kT} \left[ \frac{\Delta \mathcal{V}_D}{\pi \sqrt{\ln 2}} \frac{g_u}{B_T} a NA_t L \right]^{1/2} , \quad [78]$$

in units of watts/cm.<sup>2</sup> ster. The  $10^7$  factor in the denominator of each equation is a result of conversion from ergs/sec. to watts.

The value of  $N$  at the intersection point, i.e.,  $N_i$ , can be found by equating equation [185] for  $A_T$  for small  $k_O^*L$  to equation [187] for  $A_T$  for large  $k_O^*L$ . The same value of  $N_i$  as derived in the text results.

## APPENDIX H

### Effect of Multiple Lines on Measured Absorbance

For the Na 5890, 5896 Å. doublet

$$K_1 I_1^0 / K_2 I_2^0 = K_1 \mathcal{J}_1 / K_2 \mathcal{J}_2 , \quad [188]$$

and

$$k_1^0 L / k_2^0 L = \mathcal{J}_1 / \mathcal{J}_2 , \quad [189]$$

where  $I_1^0$  and  $I_2^0$  are the source intensities of lines 1 and 2, and  $k_1^0$  and  $k_2^0$  are the atomic absorption coefficients at the line centers of lines 1 and 2. The fractions  $\mathcal{J}_1$  and  $\mathcal{J}_2$  are given by

$$\mathcal{J}_1 = \frac{g_1}{g_1 + g_2} , \quad [190]$$

and

$$\mathcal{J}_2 = \frac{g_2}{g_1 + g_2} . \quad [191]$$

The correctness of the relationships expressed in equations [190] and [191] can be seen from equations [85], [86], and [106]. From these equations it follows that

$$K_1 \mathcal{J}_1 / K_2 \mathcal{J}_2 = K_1 g_1 / K_2 g_2 = K_1 I_1^0 / K_2 I_2^0 , \quad [192]$$

and

$$\mathcal{J}_1 / \mathcal{J}_2 = g_1 / g_2 = k_1^0 L / k_2^0 L . \quad [193]$$

The source intensities of lines 1 and 2 are given by

$$\kappa_1 I_1^0 = \mathcal{F}_1(\kappa_1 I_1^0 + \kappa_2 I_2^0) = \mathcal{F}_1 I^0, \quad [194]$$

$$\kappa_2 I_2^0 = \mathcal{F}_2(\kappa_1 I_1^0 + \kappa_2 I_2^0) = \mathcal{F}_2 I^0, \quad [195]$$

where  $I^0$  is the sum of the source intensities of lines 1 and 2 (actually source intensity after passing through the flame cell containing aspirated solvent) corrected for their relationship to the slit function. Similarly the absorbance of lines 1 and 2 is given by

$$k_1^0 L = \mathcal{F}_1(k_1^0 L + k_2^0 L) = \mathcal{F}_1 k^0 L, \quad [196]$$

$$k_2^0 L = \mathcal{F}_2(k_1^0 L + k_2^0 L) = \mathcal{F}_2 k^0 L, \quad [197]$$

where  $k^0$  is the sum of the absorption coefficients of the two lines.

The transmitted intensities with sample aspirated of lines 1 and 2 are given by

$$\kappa_1 I_{t1} = \kappa_1 I_1^0 e^{-\rho_1 k_1^0 L} = \mathcal{F}_1 I_1^0 e^{-\rho_1 k^0 L}, \quad [198]$$

$$\kappa_2 I_{t2} = \kappa_2 I_2^0 e^{-\rho_2 k_2^0 L} = \mathcal{F}_2 I_2^0 e^{-\rho_2 k^0 L}, \quad [199]$$

where  $I_{t1}$  and  $I_{t2}$  are the transmitted intensities of lines 1 and 2, and  $\rho_1$  and  $\rho_2$  are the correction factors for hyperfine structure of lines 1 and 2.

The total transmitted intensity,  $I_t$ , must equal the sum of the transmitted intensities. Therefore,

$$I_t = \kappa_1 I_{t1} + \kappa_2 I_{t2}, \quad [200]$$

and

$$I_t = \int_1 I^0 e^{-\rho_1 \zeta_1^{k^0 L}} + \int_2 I^0 e^{-\rho_2 \zeta_2^{k^0 L}} . \quad [201]$$

Expanding the exponential term one obtains

$$I_t = I^0 [ \int_1 (1 - \rho_1 \zeta_1^{k^0 L} + \dots) + \int_2 (1 - \rho_2 \zeta_2^{k^0 L} + \dots) ], [202]$$

$$I_t = I^0 [ \int_1 -\rho_1 \zeta_1^{2 k^0 L} + \dots + \int_2 -\rho_2 \zeta_2^{2 k^0 L} + \dots ] , \quad [203]$$

$$I_t \cong I^0 [ \int_1 + \int_2 - (\rho_1 \zeta_1^2 + \rho_2 \zeta_2^2)^{k^0 L} ] . \quad [204]$$

Because  $\int_1 + \int_2 = 1$

$$I_t \cong I^0 [ 1 - (\rho_1 \zeta_1^2 + \rho_2 \zeta_2^2)^{k^0 L} ] , \quad [205]$$

or  $I_t$  is given approximately by

$$I_t = I^0 e^{-(\rho_1 \zeta_1^2 + \rho_2 \zeta_2^2)^{k^0 L}} . \quad [206]$$

The difference between  $I^0$  and  $I_t$  is given by

$$I^0 - I_t = 1 - e^{-(\rho_1 \zeta_1^2 + \rho_2 \zeta_2^2)^{k^0 L}} , \quad [207]$$

and by comparison with equation [105] it may be seen that  $\Theta$  is given

by

$$\Theta = \rho_1 \zeta_1^2 + \rho_2 \zeta_2^2 . \quad [208]$$



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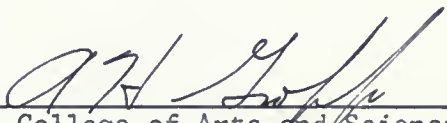
## BIOGRAPHICAL SKETCH

Thomas Joseph Vickers was born March 29, 1939, at Miami, Florida. In June, 1957, he was graduated from St. Theresa High School, Coral Gables, Florida. In May, 1961, he received the degree of Bachelor of Science, cum laude, from Spring Hill College, Mobile, Alabama. In 1961 he enrolled in the graduate school of the University of Florida. His graduate study has been supported by a Woodrow Wilson Fellowship and a National Science Foundation Cooperative Fellowship. From September, 1961, until the present time he has pursued his studies toward the degree of Doctor of Philosophy.

He is married to the former Mary Ann Coomes of Coral Gables, Florida. He is a member of the American Chemical Society and Alpha Sigma Nu honorary fraternity.

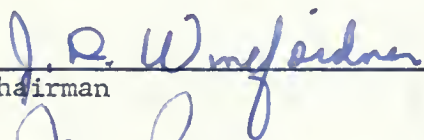
This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

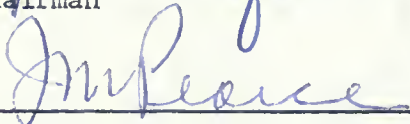
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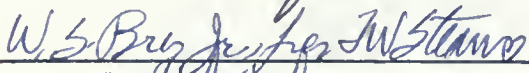
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